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ELECTRONIC STRUCTURE OF ATOMS AND MOLECULES

JOHN C. SLATER

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SOLID-STATE AND MOLECULAR THEORY GROUP
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASSACHUSETTS

Technical Report No. 3

ELECTRONIC STRUCTURE OF ATOMS AND MOLECULES

John C. Slater

SOLID-STATE AND MOLECULAR THEORY GROUP
Massachusetts Institute of Technology
Cambridge, Massachusetts

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February 15, 1953

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PREFACE

This report represents the notes of an advanced course which the writer has offered at the Massachusetts Institute of Technology during the first semester of the academic year 1952-53. A continuation of this course during the second semester will deal with the electronic structure of solids, treated from the same general point of view, and it is hoped that a companion report will be issued later, representing the notes of the second term's work. The course was intended for students who had already taken a first course in the quantum theory of atoms, molecules, and solids, and has carried many aspects of the field up to the limits of what we now know. It was designed very much with the needs of those going into the Solid-State and Molecular Theory Group at M.I.T. in mind, and the notes which form the present report are intended for guidance of those starting research along the lines now being pursued by that Group. It was felt that the readers of the Quarterly Progress Reports of the Group might well be interested in this material, which presents in a more connected fashion many of the ideas which have been mentioned in a cursory way in the Progress Reports, and for that reason these notes have been collected into a Technical Report, which is being sent to the same distribution list as the Quarterly Progress Reports.

It should be emphasized that this does not in any way represent a finished book on the subject. The typing and planographing have gone ahead in parallel with the writing, so that there has been no opportunity to revise earlier parts of the notes to take advantage of ideas presented in later sections. In many cases the writer's ideas have become changed or clarified as the writing, and the giving of the course, have proceeded. In many cases problems have been talked over with members of the Solid-State and Molecular Theory Group, and a great deal of thanks is due to many of them for help in clarifying or in originating some of the ideas. In spite of the preliminary nature, nevertheless, the subject is advancing at such a rate that the writer feels that a presentation such as this will help speed up the progress, both at M.I.T., and at other places where similar work is under way.

It will be clear to the reader that the material presented here is not in any sense an explanation of molecular structure on the basis of quantum mechanics. It is rather an exploration of the methods by which quantum mechanics can hope to solve the problems posed by molecular structure. Only when these methods are better understood, by the study of the sort of simple molecules treated here, can we hope to proceed to more complicated cases. The writer feels that the understanding of chemical problems according to the quantum theory has been set back, rather than advanced, by the great desire which many scientists have had to derive numerical results on the basis of inadequate approximations and unjustified use of simplified theories. It is his hope that, by encouraging a more careful study along the lines of those outlined here, we may eventually find what sort of simplifications really are justified, and thus be led eventually to a theory of the more complicated molecules which is at the same time simple enough to use and to understand in a qualitative way, and yet accurate enough and well enough based on the quantum theory to be reliable. He does not feel that the theory of molecular structure has yet reached that fortunate state.

John C. Slater

Cambridge, Mass.
February, 1953

CHAPTER 1

THE DETERMINANTAL METHOD FOR ATOMS

In these lectures we shall treat the problem of the motion of n electrons, under the action of their mutual Coulomb repulsions, the attractions of the nuclei of the atoms of the system, and such mutual magnetic forces, and external electric and magnetic fields, as may be present. Nuclei will be assumed to be fixed in position, so that the energy levels of the system will be functions of the nuclear positions, regarded as parameters. According to the fundamental theorem of Born and Oppenheimer,(1) these energies can then be used as a potential function for a treatment of the motion of the nuclei. It is justified to separate electronic and nuclear motion in this way, up to a certain approximation. The approximation breaks down where the nuclei are moving so fast that their interaction with the electrons is able to cause electronic transitions from one electronic stationary state to another; but we neglect such problems in these lectures.

We let the three space coordinates of the ith electron be symbolized by x_i, and its spin coordinate by s_i.(2) We let the wave function of the n electrons be $U(x_1 s_1 x_2 s_2 \cdots x_n s_n)$, where we assume that the time has already been eliminated. Then, if we disregard magnetic terms (as we shall almost always do), and if we have no external fields, the Schrödinger equation for U is

$$\left\{\sum(i)\left(-\nabla_i^2\right) - \sum(i,a)\left(\frac{2Z_a}{r_{ia}}\right) + \sum(\text{pairs } i,j)\left(\frac{2}{r_{ij}}\right) + \sum(\text{pairs } a,b)\left(\frac{2Z_a Z_b}{r_{ab}}\right)\right\}U = EU. \quad (1.1)$$

Here we have used atomic units, in which the unit of length is the Bohr radius of hydrogen, and the unit of energy is the Rydberg.(3) The Laplacian operator $-\nabla_i^2$, operating on the coordinates x_i is the kinetic energy of the ith electron. The term $-2Z_a/r_{ia}$, where Z_a is the charge on the ath nucleus, in electronic units, r_{ia} is the distance from i^{th} electron to a^{th} nucleus, is the Coulomb attraction between i^{th} electron and a^{th} nucleus. The factor 2 arises from the atomic units. The summation is over all n electrons, and over all nuclei. The next term, the summation of $2/r_{ij}$, represents the Coulomb repulsions between all pairs of electrons. The final term, the summation of $2Z_aZ_b/r_{ab}$, represents the Coulomb repulsions between nuclei. Since the nuclear positions are regarded as fixed, it is a constant as far as Schrödinger's equation is concerned, but we shall need it when we consider the total energy of the system. We shall call the complete Hamiltonian oper-

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[1] M. Born and J. R. Oppenheimer, Ann. Physik 84, 457 (1927); for a simplified treatment of this result, see J. C. Slater, Quantum Theory of Matter (McGraw-Hill, New York) 1951, pp. 500-501. Future references to this work will be merely indicated as QTM.

[2] For the meaning of this spin coordinate, see QTM, pp. 187-192.

[3] For these units, see QTM p. 110. Note that they are different from the atomic units used by Hartree and his school, in which the unit of energy is two Rydbergs. Hartree's choice of units removes the factor 2 in the potential energy terms in Eq. (1.1), but introduces a factor 1/2 in the kinetic energy term.

ator on the left side of Eq. (1. 1) H.

Our whole problem in these lectures is the solution of Eq. (1. 1). Except in the simplest cases, it is hopeless to consider an exact solution, and we are forced to approximations. The determinantal method, the subject of our lectures, represents the most generally useful of such approximations. Before we introduce it, let us thoroughly convince ourselves that an exact solution is impossible. Surely we cannot hope for an analytic solution, so that we are at once forced to consider numerical solutions. Our wave function, disregarding spin, is a function of 3n variables. But no one of the high speed computing machines now available or contemplated can solve partial differential equations with more than two variables. Thus no such machine could compute our function. The limiting factor in these machines is storage of information, and this same factor would limit our numerical calculation of the wave function U, no matter what method of computation were used. We can hardly make a usable table of values of a function of one variable with less than 100 entries. For a function of 3n variables, then, we should need a table with $(100)^{3n} = 10^{6n}$ entries. That is, for one particle we should need a million entries, for two particles 10^{12}, and so on. All the books in the world would not be enough to write down the wave function for a single heavy atom, and all the magnetic tape we can conceive of would not record the information. The direct approach to a numerical calculation of a Schrödinger equation for an atomic or molecular system is, then, completely impossible. We must look for other methods of handling it.

Our best hope is to express the wave function approximately, in terms of a number of functions of a smaller number of variables, which we can either tabulate or express analytically. The determinantal method expresses the function U in terms of a number of functions u_i of the coordinates of a single particle, and of spin. These functions u_i are called one-electron functions, or orbitals. We have seen that a minimum of a million entries in a table would be required to express a function of three variables, and while this is an appalling thing to contemplate, it is not completely out of the question, and maybe someday such functions will be handled numerically. For the present, however, we cannot handle them numerically, and must use partly analytical methods. The thing that is almost always done in practice is to assume that the u_i's are linear combinations of solutions of a one-electron Schrödinger equation for a central field problem, which we know by elementary methods are products of a spherical harmonic of angle, and a function of the radius vector. This function of the radius vector must be determined numerically, if we are dealing with an arbitrary central field problem, but we are left with a function of only one variable to work out and write down numerically, and this can be done with 100 entries in a table, or actually very satisfactorily with some 300 entries. It is then no problem at all to deal with a number of such functions of radius. Quite a number of such functions are needed, but the number is comparable with the number of electrons in the problem, or in the case of a large sample of matter, comparable with the number of electrons in an atom rather than in the whole sample. The necessary numerical information to express an approximate solution of a problem by this method is no more than can go into a journal article of moderate size. We shall now go on to state the determinantal method, which leads to this great simplification, but at the expense of giving only an approximate solution.

1. History of the Determinantal Method

Before stating the details of the determinantal method, it is worthwhile giving a little of its history, and of the history of the whole effort to solve the many-body problem in quantum mechanics. This history begins in the time of the older quantum mechanics, before 1926 when the wave mechanics was developed. After Bohr's success in 1913 with the theory of the hydrogen atom, it was only natural that the thoughts of many physicists turned to the problem of heavier atoms. An inherent difficulty arose at once. The older quantum theory was based entirely on classical mechanics: it postulated that particles obeyed classical mechanics, but with quantum conditions superposed on it. These quantum conditions were stated in a form applicable only to motions of a multiply periodic character.(4) And yet enough was known about classical mechanics to realize that the many-body problem did not have multiply periodic solutions, aside from very exceptional cases. Fruitless attempts were made to set up models of light atoms, particularly helium, which would have multiply periodic motion; for instance, a model of helium consisting of two electrons rotating at opposite ends of a diameter in the same circular orbit. A number of such models were tried, none leading to anything like agreement with experiment. It was clear that something radically different was needed.

The radically new idea came from Bohr. It had already become clear, by much study of optical and x-ray spectra on the part of a great many workers,(5) that many of the facts of spectroscopy could be interpreted if we identified the energy levels with those of a single electron moving in a central field, such as would be set up by the nucleus and a collection of electrons surrounding it. Bohr(6) took the radical step of assuming that an electron in a penetrating orbit moved all the way from the outer to the inner part of the atom, ploughing its way through inner electronic orbits, and that still the other elec-

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[4] These quantum conditions, and the older quantum mechanics, are developed in the papers of Bohr and Sommerfeld in the 1920's. A very good and complete account of the theory, published just before the wave mechanics was developed, is given in M. Born, Vorlesungen uber Atommechanik, Vol. 1 (Springer, Berlin) 1925.

[5] This development is well described by A. Sommerfeld, Atombau und Spektrallinien, Fourth Edition (Vieweg, Braunschweig) 1924. The Third Edition, 1922, was translated into English and published by Dutton under the title Atomic Structure and Spectral Lines.

[6] N. Bohr, Z. Physik 9, 1 (1922); Ann. Physik 71, 228 (1923); The Theory of Spectra and Atomic Constitution (Cambridge University Press) 1922 (Second Edition, 1924); N. Bohr and D. Coster, Z. Phys. 12, 342 (1923).

trons exerted a field on it qualitatively as if they were arranged statically around the nucleus. This was clearly entirely outside the framework of the simple multiply periodic orbits that had been contemplated by the quantum theory up to then, and from the time of these suggestions it was clear to physicists that the older quantum theory could not be correct for such problems. But the picture qualitatively led to many valuable results: the structure of the periodic table, the nature of the x-ray levels, and the general understanding of optical spectra.

Bohr did not try to set up a self-consistent field, though the general idea was plainly in his mind. Several other workers made efforts in this direction, however, during the period of the older quantum theory. Thus calculations were made by Schrödinger,(7) Fues,(8) van Urk,(9) Hartree,(10) Sugiura and Urey,(11) and Lindsay,(12) all trying to set up potentials for central fields in which a moving electron would have term values agreeing with observed values. They succeeded very well for several simple spectra, and the resulting fields are close to those which we now know as self-consistent fields for the same atoms. They fully realized the desirability of self-consistency; that is, of deriving the potential from the charge distribution of the electrons. Fues and Lindsay made some efforts to carry out the requirement of self-consistency. However, with the older quantum mechanics, in which the electrons moved in discrete orbits, it was obviously a very artificial matter to average out to get a central field, and this made all efforts at self-consistency very unsatisfactory.

This situation was entirely changed, however, as soon as Schrödinger(13) introduced the wave mechanics. Then it became clear that the inner electrons really had a continuous charge distribution, and it was a very obvious step to determine the potential of this charge distribution, and to assume that the outer electron moved in this potential field. Hartree(14) returned to the problem immediately, and started his long series of self-consistent field calculations, assuming that each electron moved in the field of all other electrons of the atom, averaged over directions to get spherical symmetry. He found, as is well known, one-electron energy levels in very good agreement with observed term

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[7] E. Schrödinger, Z. Physik 4, 347 (1921).

[8] E. Fues, Z. Physik 11, 364 (1922); 12, 1 (1922); 13, 211 (1923).

[9] T. van Urk, Z. Physik 13, 268 (1923).

[10] D. R. Hartree, Proc. Cambridge Phil. Soc. 21, 625 (1923).

[11] Y. Sugiura and H. C. Urey, Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd. 7, No. 13 (1926).

[12] R. B. Lindsay, J. Math. Phys., M.I.T., 3, 191 (1924).

[13] E. Schrödinger, Ann. Physik 79, 361, 489 (1926); 80, 437 (1926); 81, 109 (1926); Phys. Rev. 28, 1049 (1926).

[14] D. R. Hartree, Proc. Cambridge Phil. Soc. 24, 89, 111 (1928), and many further papers which will be referred to later.

values, both optical and x-ray, and wave functions whose correctness could be checked by computing x-ray form factors and in various other ways. Hartree's procedure was set up intuitively, not as a result of any straightforward effort to solve the many-body Schrödinger equation, but it was clear that it gave one-electron wave functions for the various electrons which had some very close connection with the real solution of the problem.

The present writer(15) tried to investigate this connection in the following way. Hartree had found one-electron functions u_i for the various electrons. The present writer set up a product of such functions, each referring to a different electron, as $u_1(x_1)u_2(x_2)$ . . $u_n(x_n)$, to represent a many-dimensional wave function. If the electrons were really statistically independent of each other, acting on each other only on the average, this would be a correct wave function. He then allowed the Hamiltonian operator H for the atom, as given in Eq. (1.1), to operate on this wave function, and found the diagonal energy, the integral $\int U^* H U \, dx_1 \ldots dx_n$, which should represent the energy of the system. This energy cannot be checked experimentally, in most cases, but the ionization potentials can. Thus we must calculate also the energy of the ion with one electron removed. The writer used the same orbitals for the ions as for the atom, simply omitting the function $u_k(x_k)$ referring to the electron removed, and calculated the energy of the ion, making an estimate of the error involved in using the same functions u_i for the ion as for the atom, in spite of the fact that there should really be some rearrangement of charge in going from the atom to the ion, and hence some modification of the wave functions. This change, being a first-order change in the wave functions, makes only a second-order change in the energy, by elementary principles of perturbation theory, and these second-order corrections were estimated. The final result was that the ionization potential, as calculated by this correct method involving the wave function and energy operator of the whole atom, should agree closely with the one-electron energy parameter, as Hartree had found that it did. This was an anticipation of the result of Koopmans,(16) derived from the Hartree-Fock method, which we shall discuss later. It might be mentioned that in the paper by the writer just referred to, corrections for exchange were considered, as derived on the basis of the group theory, though they do not follow directly from the product form of wave function $u_1(x_1)$ . . $u_n(x_n)$, and though the determinantal form of function was not yet in use for this purpose.

To follow our history of the determinantal method, we must now go back and consider another development which started out quite separately from the self-consistent field method, namely the theory of complex spectra, and the electron spin and exclusion principle which were closely entwined with it. During the time up to 1925, the theory of

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[15] J. C. Slater, Phys. Rev. 32, 339 (1928).

[16] T. Koopmans, Physica 1, 104 (1933).

complex spectra, as described for instance in the work of Sommerfeld referred to earlier, made very great progress. Regularities were discovered, particularly by use of the Zeeman effect, quantum numbers were introduced, the Landé interval rule and various other partial formulations of the problem were introduced, on the basis of simple ideas of space quantization. But up until 1925, great puzzles and complications were present in the theory, on account of the fact that the electron spin had not been discovered, and the exclusion principle had not been formulated. Thus Bohr, in his theory of the periodic system given in the papers to which we have referred, did not have the exclusion principle to work with, and in fact he gave an incorrect value for the number of electrons in a closed shell of any particular azimuthal quantum number, and did not have any convincing explanation as to why we should have closed shells at all. The incorrect assignment of electrons to shells was soon removed by Stoner,(17) who arrived from x-ray evidence at the assignment of two electrons to a shell of s electrons, six to a p shell, ten to a d shell, and so on, which we now know to be correct. He still did not have a convincing reason for these numbers, however, and it remained for Pauli,(18) in 1925, to make his famous postulate of the exclusion principle. He still was not working with the theory of the spinning electron, however; his statement of the exclusion principle is in terms of a fourth quantum number, in addition to the ordinary three quantum numbers of orbital motion, whose significance was not clear at the time, though it had been found necessary to introduce it to describe the spectra. Almost simultaneously, Uhlenbeck and Goudsmit(19) introduced the postulate of the electron spin, and the basis for the elementary theory of complex spectra was laid.

It is very interesting to see how rapidly and completely spectrum theory developed, once it had these foundations, on the basis of the vector model, but without wave mechanics. Thus Hund's(20) book, though it was published just after wave mechanics was introduced, makes almost no use of it; but it contains a description of the theory of complex spectra which is substantially like that in use at present, including complete discussion of the multiplets forbidden by the exclusion principle, and such matters, but not including the calculation of energy levels. It was a much slower process, however to make a synthesis of this theory and of wave mechanics. The first very important step in this direction was taken by Heisenberg.(21) He considered the behavior of a system consisting of two like particles. If these are first considered independent of each other, one will be described

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[17] E. C. Stoner, Phil. Mag. 48, 719 (1924).

[18] W. Pauli, Jr., Z. Physik 31, 765 (1925).

[19] G. E. Uhlenbeck and S. Goudsmit, Naturwiss. 13, 953 (1925)

[20] F. Hund, *Linienspektren und periodisches System der Elemente* (Springer, Berlin) 1927.

[21] W. Heisenberg, Z. Physik 38, 411 (1926); 39, 499 (1926), 41, 239 (1927).

by a wave function $u_1(x_1)$, a function of the coordinate x_1 of this particle, and the other will be described by $u_2(x_2)$. The product of these two will represent a wave function for the system. Heisenberg then considered the effect of an interaction between the two particles, treated as a perturbation. He noted that there are two unperturbed functions, $u_1(x_1)\, u_2(x_2)$ and $u_2(x_1)\, u_1(x_2)$, which on account of the identity of the particles are degenerate with each other, and he showed by the theory of perturbations of degenerate systems that in the perturbed problem the correct wave functions were the symmetric and antisymmetric combinations $u_1(x_1)\, u_2(x_2) \pm u_2(x_1)\, u_1(x_2)$, and that the energies of the two resulting functions differed by an amount depending on the exchange integral

$$\int u_1^*(x_1)\, u_2^*(x_2)\, H\, u_2(x_1)\, u_1(x_2)\, dx_1 dx_2 \quad ,$$

where H was the Hamiltonian operator of the problem. He also showed, but by a rather complicated way, that the symmetric function was to be associated with a singlet term in the spectrum of an atom containing two electrons, and the antisymmetric function with a triplet.

In this important work, Heisenberg laid the foundations for three later developments: the theory of complex spectra, which we shall take up at once; the theory of covalent binding, which Heitler and London(22) were soon to set up on the basis of Heisenberg's fundamental work; and the theory of ferromagnetism,(23) which Heisenberg himself set up. The theory of complex spectra, on the basis of wave mechanics, however, did not develop as fast as one might have hoped. In one of Heisenberg's papers, quoted above, he started the generalization of the problem of two electrons to the problem of many electrons. He had realized in his first paper the relation between an antisymmetric function and the exclusion principle, and he generalized this in the later paper by setting up an antisymmetric combination of the orbitals $u_1 \dots u_n$ of an n-electron problem, forming a determinant (though he did not write it in determinantal form). At the same time, Dirac(24) had independently arrived at the same results as Heisenberg regarding the symmetric and antisymmetric solutions in a problem of two particles, the use of a determinantal function to express the antisymmetric combination in a problem of n electrons, and its relation to the exclusion principle. But the reason why these generalizations did not proceed faster was the complication introduced by the electron spin.

The wave functions which Heisenberg and Dirac were using were functions of coordinates alone, not of spin; Pauli(25) had not yet introduced his spin matrices, which gave a practical method of setting up wave functions including spin. Heisenberg realized

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[22] W. Heitler and F. London, Z. Physik 44, 455 (1927).

[23] W. Heisenberg, Z. Physik 49, 619 (1928).

[24] P. A. M. Dirac, Proc. Roy. Soc. (London) 112, 661 (1926).

[25] W. Pauli, Jr., Z. Physik 43, 601 (1927).

that in a case where all spins were parallel, a single determinant of orbitals formed the correct antisymmetric wave function; but the idea of antisymmetry in cases where some spins were pointing one way, some the other, could not be easily introduced. Lacking that, Heisenberg was forced to consider the general behavior of a combination of products of orbitals under a permutation operation; the antisymmetric combination changes sign, the symmetric combination is unchanged, but other combinations can be transformed into each other. This led naturally to a discussion by means of the group theory, as applied to the permutation group. This resulted in a great development of the group theory, in which Wigner,(26) Hund,(27) Heitler,(28) and others took part, as well as Heisenberg. The development was complicated, but not fruitful. Those engaged in it became immersed in their mathematics, and failed to make connections with the theory of complex spectra already so well developed from the vector model point of view. The step which they were missing was the combination of Pauli's treatment of the spin, and the determinantal method of setting up antisymmetric wave functions.

This missing step was supplied by the present writer in 1929.(29) In this paper, one-electron wave functions were set up which involved spin, using the general ideas of Pauli, as well as coordinates. Every wave function allowed by the Pauli exclusion principle then had to be an antisymmetric combination of one-electron functions, so that every such function could be written as a determinant,

$$\begin{vmatrix} u_1(x_1s_1) & u_1(x_2s_2) & \dots & u_1(x_ns_n) \\ u_2(x_1s_1) & u_2(x_2s_2) & \dots & u_2(x_ns_n) \\ \dots & \dots & \dots & \dots \\ u_n(x_1s_1) & u_n(x_2s_2) & \dots & u_n(x_ns_n) \end{vmatrix} \qquad (1.2)$$

Each such determinantal function could be identified with one of the assignments of quantum numbers to electrons, which was the basis of the methods already developed for treating complex spectrum theory,(30) and it was possible to take over the whole of that theory bodily into the framework of wave mechanics. It was also possible, in addition, to go much further, for now the matrix components of energy with respect to a set of determinantal wave functions could be computed, and the secular equations solved, yielding the correct combinations of determinants to represent the various actual stationary states of the problem. In this way the energy separations of the various terms could be computed.

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[26] E. Wigner, Z. Physik 40, 492 (1926); 40, 883 (1927).

[27] F. Hund, Z. Physik 43, 788 (1927).

[28] W. Heitler, Z. Physik 46, 47 (1928).

[29] J. C. Slater, Phys. Rev. 34, 1293 (1929).

[30] These methods are described, for instance, in Hund's book already quoted; they are taken up in QTM, pp. 158-182.

The connection with Hartree's self-consistent field was obvious: the one-electron functions u_i were chosen to be a product of a Hartree function of coordinates, and a Pauli function of spin. With this development, the determinantal method was complete, and it has formed the basis of most subsequent development of the theory of atoms, molecules, and solids, as we shall later describe. It should be mentioned, however, that at about the same time, Dirac[31] approached similar problems from a different point of view, which yielded results which can also be used to discuss the same type of problem. We shall make little use of these methods of Dirac in the present lectures, but they have been taken up to a considerable extent by the workers in the theory of magnetism.

2. The Determinantal Method

The determinantal method is very simple in principle. We set up a number of determinants of the nature of that given in Eq. (1. 2), and try to make a linear combination of them which equals the correct wave function of the problem, or solution of Eq. (1. 1), to an adequate approximation. There are then two major problems connected with the method. The first is how to set up the determinants in the first place; that is, what orbitals u_i to use. The second is, having set up the determinants, how to find the correct linear combination of them. This second question is straightforward, and the answer is obvious from elementary quantum mechanics. We find the matrix of the energy operator H, of Eq. (1. 1), between the various determinantal functions, and then make linear combinations of these functions which diagonalize the energy. The problem is only to compute the matrix components of energy; then the rest of the work is straightforward, involving the solution of a secular equation. The first question, the determination of the proper orbitals u_i, however, is much more subtle and difficult. We shall have a good deal to say about it in the future. Before passing on to the second question, however, it will be worthwhile to indicate some of the factors underlying the choice of the u_i's.

In the first place, we must answer the question, whether to approximate our solution by a single determinant, or to use many such determinants. For a problem in which all electrons are in closed shells, a passably good approximation can be made using only a single determinant. For problems in which there are multiplets arising from electrons outside closed shells, this cannot be done at all, and we must use a combination of a number of determinants. In any case, a single determinant, or a few determinants, will not give a good approximation, for the true wave function certainly does not take this form, on account of the large interaction between electrons. If we wish to do our best with a single determinant, however, then we have a straightforward way to choose the u_i's: we make use of the variation principle, by which it can be shown that the true wave functions of the problem are those for which the energy integral $\int U^* HU \, dx_1 \ldots dx_n$ is stationary, when we vary U, provided U is kept normalized. We can interpret this as meaning that if we start with a single determinantal function for U, and vary the u_i's, we shall get the best approximation to the true wave functions if we make the energy integral stationary with respect to variations of the u_i's, and in particular, the best approximation to the ground state is obtained if the energy integral is minimized. This condition leads to the Hartree-Fock equations, which we shall discuss in a later section. Since they deal with only a single determinantal function, containing just n orbitals u_i, this method determines only those n orbitals, and does not lead to any method of finding additional ones.

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[31] P. A. M. Dirac, Proc. Roy. Soc. (London) 123, 714 (1929).

Quite a different problem arises if we are willing to use a combination of many determinants. We can see this by considering the limiting case, where we are willing to use an infinite number of determinants. These can be chosen to form a complete orthogonal set of n-electron antisymmetric functions of coordinates and spins. This can be accomplished by making the set of u_i's a complete orthogonal set of one-electron functions. Then by general principles of quantum mechanics we know that any antisymmetric function of the coordinates and spins of n electrons can be expressed as a linear combination of such a complete orthogonal set, so that our problem can be solved exactly, and it makes no difference what complete orthogonal set we use. Of course, this limiting case of an infinite number of determinants does not concern us in practice. What we may well be interested in, however, is the problem of finding a finite number of determinants, such that an appropriately chosen linear combination of them forms a very good approximation to the solution of the problem.

The choice of this finite set of determinants is a matter of insight, and we shall have much to say about it in the future. Briefly, however, if we choose the u_i's to represent solutions for the occupied, and lower unoccupied, levels of the atoms, then the linear combination of determinants will represent a problem of interaction of a few lower configurations of the problem, and the wave function arising in this way may be expected to be fairly good, at least when our major interest is in the energy differences between the states of these configurations. Let us suppose that, by such arguments, we have set up a number of determinants. Then our problem is to solve the secular equation arising from these determinantal functions. We may reduce the order of this equation a good deal by taking full advantage of the symmetry and multiplicity properties of the wave functions; we shall find in many cases that there are no non-diagonal matrix components of energy between determinantal functions of different symmetry and multiplicity properties. But we are still likely to be left with secular equations of rather high order to be solved.

Three methods may be thought of for solving these secular equations. In the first place, in the original paper on complex spectra, by the present writer, much use was made of the diagonal sum rule, and similar subterfuges, which made the direct solution of the secular equation almost unnecessary. Such devices are available in simple cases, but we must not count on them, and shall not stress them in these lectures. Secondly, there is the well-known method of perturbation theory. This is appropriate if one of the determinantal functions is a very good approximation to the solution we are seeking, and the others appear only with very small coefficients in the final combination. This situation can sometimes be achieved, but again we cannot count on it. Finally we are left with the straightforward method of the numerical solution of the secular equation. Until very recently, this was so difficult as to be out of the question. Now, however, with the rapid development of high-speed digital computers, it becomes possible. Secular equations involving up to twelve determinants have recently been solved by this method,(32) and the computers are improving so rapidly that it will not be long before considerably greater secular equations can be attacked. One gets the feeling, therefore, that the future development of the method is likely to use more and more determinants, and to rely completely on high-speed computers to solve the resulting secular equations.

The final result of the solution of such a secular equation is a set of energy values, and of transformation coefficients for finding the correct wave functions as linear combinations of the original determinantal functions. This is a rather small set of numbers, and if the orbitals out of which the determinantal functions are computed can be described analytically, or numerically by simple tables of values, we have reduced the problem of describing the wave function, from the formidable proportions mentioned earlier, to a manageable scale. If we use this method, there is no particular advantage in having one of the determinants of our set represent the wave function to great accuracy. We can just as well use a linear combination in which many wave functions have coefficients of large size. The essential feature of the u_i's, in this case, is that the whole set of determinants formed from them should be capable of describing the correct function with good accuracy. We can state this criterion more clearly if we remember that a wave function can be represented as a vector in a function space of an infinite number of dimensions. Suppose we have N determinantal functions. If they are linearly independent, they will define an N-dimensional sub-space in this function space. We may now supplement our N vectors with an infinite set of others, orthogonal to all the N we started out with, so that all taken together will form a complete set. Now our wave function, which we are trying to determine, is also represented by a vector. This can be represented exactly as a linear combination of our original N vectors, provided its scalar product with any one of the additional vectors of the complete set, not included in the original N, is zero. That is, in this case the vector lies in the N-dimensional sub-space defined by our vectors. This is the situation we try to achieve by our choice of a finite number of determinantal functions. If we have almost achieved it, that is, if the scalar products of the correct vector with all vectors not in our original set of N are small, then we shall have

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[32] A. Meckler, Ph.D Thesis, M.I.T., September, 1952, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., July 15, 1952.

a good approximation. As we have said, it is a matter of insight to choose our N determinants to achieve this situation, and we shall give much discussion, as we go on to methods of doing it.

Let us suppose such a set of determinants to be set up, however, and now let us address ourselves to the other part of our problem, that of determining the correct linear combinations of determinants. To do this, as we have mentioned, we must find the non-diagonal matrix components of the Hamiltonian with respect to these functions, and set up the usual determinantal equation between them. At the outset, we observe one thing: our procedure will be very greatly simplified if the determinantal functions are orthogonal to each other. This simplification is just like that found in algebra and analytic geometry, in which it is very easy to manipulate problems if they are expressed in rectangular coordinates, but very complicated in an oblique coordinate system. The equations can be set up in non-orthogonal systems, and they have been so set up;(33) but they have almost never been used, and in actual applications it has almost always been assumed that the departures from orthogonality are small, and these departures are then neglected. This is not justifiable. We shall prefer to use determinantal functions which are really orthogonal, and to use these rigorously. We shall set up our equations only for this case, and shall carefully avoid all use of non-orthogonal determinants, unless we specify otherwise in special cases.

It is easy to prove that all our determinantal functions will be orthogonal to each other, provided every one-electron orbital appearing in any one of the determinants is orthogonal to every other one; and we shall generally make this assumption. There are a number of consequences from this assumption, which we might not quite realize at first, and a number of comments to be made about it. In the first place, it excludes the use of the ordinary Hartree functions as orbitals u_i. Hartree's original method is based on the assumption that each electron moves in the field of all electrons except itself. This means that each wave function is a solution of a different central field problem, so that there is no reason why they should be orthogonal, and in general they are not. It does not exclude functions determined by the Hartree-Fock method; we shall show later that, even though these are solutions of different central field problems, still they automatically are orthogonal to each other. But we have noted that since the Hartree-Fock method operates only with a single determinantal function, it determines only n orbitals u_i. If we want to use a number of determinantal functions, we must have more u_i's. If we found more of these from a second Hartree-Fock problem, referring perhaps to a different configuration from the first, all the u_i's derived from this second problem would be somewhat different from those of the first set. To see this physically, let us suppose that the

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[33] See, for instance, J. C. Slater, Phys. Rev. 38, 1109 (1931), where they are discussed for molecular problems.

first Hartree-Fock problem represented the ground state of an atom consisting of closed shells (for instance an inert gas atom), and the second problem an excited configuration (for instance the same atom in which the two s electrons in one of the shells were excited into s states in a higher, previously unoccupied shell). The excitation of these electrons would affect all the other electrons of the atom, even down to the K shell, so that the second set of u_i's, as we have said, would all be different from the first. But then they would not be orthogonal to the functions of the first set, and the convenience of our method would be lost.

We wish, then, to construct all our determinantal functions from one single set of orthogonal orbitals u_i, choosing n of them for the first determinant, another n for another, and so on. Thus if we have N orbitals, we shall be able to choose the n from them in $N!/\left\{n!(N-n)!\right\}$ ways, and we shall be able to set up this number of determinantal functions from them. There are really two practical ways of finding the set of N orthogonal orbitals. One is to have them all given as solutions of a single Schrödinger equation for the motion of a single particle; for we know that all solutions of a single Schrödinger problem are orthogonal to each other. A practical way to do this, as solutions of a Schrödinger problem which respresents a self-consistent field in a satisfactory way, has recently been given by the present writer;(34) we shall discuss this method in detail later. The second method is to set up functions which we have artificially made orthogonal. If we have any N non-orthogonal vectors, then we can set up N linear combinations of them, which will be orthogonal, in an infinite number of ways. Thus if we have two vectors in a plane which are not at right angles, (and also not parallel), we can set up any two vectors in the plane which are orthogonal to each other, and they can be written as linear combinations of the first two. Now we can prove a very important general theorem: if we have two sets of N linearly independent vectors, of the sort just described, one set being derived from the other by linear transformations, and if we form all the determinantal functions from each set of N orbitals, choosing n functions for each determinant, then the determinantal functions of one set are linear combinations of the determinantal functions of the other set. Thus an approximate solution of Schrödinger's equation which can be expressed as a linear combination of functions of the first set can equally well be expressed as a linear combination of functions of the second set. The final result of our calculations will then be the same, in either case. Since it simplifies the calculation greatly, it is therefore worthwhile, if we wish to start with N non-orthogonal vectors or orbitals, to make N orthogonal linear combinations of them at the outset, and then proceed from there. We shall later discuss certain methods of making these linear combinations which have particular value in simplifying the later steps of the calculation. But once we have done this, we then wish to solve the secular problem in which all u_i's are

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[34] J. C. Slater, Phys. Rev. 81, 385 (1951).

orthogonal, as we stated somewhat earlier, so that we are justified in limiting our calculation of the matrix components of energy to this simple case. We note that the simplest result of the theorem mentioned in this paragraph is that if N = n, or if we have just as many orbitals as electrons, so that only one determinant is formed, this determinant will be identical whether it is formed from the original n orbitals, or from any n linearly independent linear combinations of them.

We have now discussed the general philosophy of the determinantal method enough so that we are prepared to proceed with its use. We shall then calculate the matrix components of the energy between two such determinantal functions, formed from two different selections of n orbitals out of a set of N orthogonal (and normalized) orbitals. We shall assume each determinant to be divided by $(n!)^{1/2}$; then the determinants will be normalized, as well as orthogonal, as a consequence of the orthonormal properties of the u_i's. Then it is a straightforward matter to compute the required matrix components, and we merely state the results.(35)

3. Matrix Components of Energy and Angular Momentum

The energy operator, given in Eq. (1.1) is a sum of operators, which we may call f_i, each operating on the coordinates of a single electron (that is, $-\nabla_i^2 - \sum(a)\, 2Z_a/r_{ia}$), and a sum over pairs of electrons of quantities g_{ij}, each equal to $2/r_{ij}$, each operating on the coordinates of two electrons; the remaining terms, the electrostatic interactions between nuclei, are a constant, and have a diagonal matrix. We then wish to find how to get the matrix components of such operators with respect to determinantal wave functions of the form given in Eq. (1.2), properly normalized by dividing by $(n!)^{1/2}$, in which we are to assume that all orbitals u_i appearing in all the determinants are orthogonal to each other. If one of the determinants is formed from orbitals $u_1 \ldots u_n$, the second from orbitals $u_1' \ldots u_n'$, then we can see very easily that the matrix of an operator like H, which is symmetrical in all the electrons, can be written in the form

$$\sum_P \int (\pm P)\, u_1'^*(x_1 s_1) \ldots u_n'^*(x_n s_n)\, H u_1(x_1 s_1) \ldots u_n(x_n s_n)\, dx_1 \ldots dx_n ,$$

where the sum is over all permutations of the subscripts 1 . . n of the first set of functions, each term is to appear with a + or - sign according as the permutation involves an even or odd number of interchanges of rows or columns, and the integration over the x's is supposed to include also a summation over the spins. If the operator H consists of summations of quantities f_i, each f_i will operate on only one of the u's following it, so that on account of orthogonality, the integral will be zero unless each u' except u_i' is identical with the corresponding u. If H consists of summations of g_{ij}'s, the integral will be zero unless each u' except the ith and j^{th} is identical with the corresponding u. Proceeding in this way, we can easily find the matrix components. These are stated in QTM, pp. 194, 195, and we repeat the definition in the same form.

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(35) The results for diagonal components were stated by J. C. Slater, Phys. Rev. 34, 1293 (1929); for non-diagonal components, by J. C. Slater, Phys. Rev. 38, 1109 (1931); note a typographical error there in the formula for a quantity called (U/G/U'). For the non-diagonal components, see also E. U. Condon, Phys. Rev. 36, 1121 (1930). The results are also given in QTM, p. 195.

To state the values of these components, let us define a quantity

$$(i/f/j) = \sum(\text{spin } 1)\int u_i^*(x_1s_1)\, f_1 u_j(x_1s_1)\, dx_1 \qquad (1.3)$$

We note that if f is an operator depending on coordinates only, as in the operator H from Eq. (1.1), then the quantity (1.3) will be zero if the functions u_i and u_j correspond to different spins. On the contrary, if f depends on spin only, the quantity will be zero if u_i and u_j correspond to different functions of coordinates. Similarly let us introduce a quantity

$$(ij/g/k\ell) = \sum(\text{spin } 1)\sum(\text{spin } 2)\iint u_i^*(x_1s_1)\, u_j^*(x_2s_2)\, g_{12} u_k(x_1s_1)\, u_\ell(x_2s_2)\, dx_1 dx_2 \qquad (1.4)$$

Here again we notice that if g_{12} depends on coordinates only, this quantity is zero unless u_i and u_k correspond to the same spin, and u_j and u_ℓ correspond to the same spin.

In terms of these symbols (1.3) and (1.4), we now find that the diagonal matrix component of energy with respect to a determinantal wave function equals

$$\sum_i (i/f/i) + \sum_{\text{pairs } i,\, j} \Big[(ij/g/ij) - (ij/g/ji)\Big], \qquad (1.5)$$

where the quantities (ij/g/ji) are called exchange integrals, and where we see that they are zero unless the orbitals u_i and u_j correspond to electrons with the same spin. The non-diagonal matrix component between two determinantal wave functions will be zero if the two determinants differ in more than two orbitals. If they differ in just two, say by having orbitals u_i and u_j replaced by u_i' and u_j', all others being common to both determinants, the non-diagonal matrix component is

$$(ij/g/i'j') - (ij/g/j'i') \,. \qquad (1.6)$$

If they differ in one orbital, u_i being replaced by u_i', all others being common to both determinants, the non-diagonal matrix component is

$$(i/f/i') + \sum_{k \neq i} \Big[(ik/g/i'k) - (ik/g/ki')\Big] \qquad (1.7)$$

By use of these formulas, we can easily find the matrix components of the energy between various determinantal wave functions, provided we can compute the integrals of form (1.3) and (1.4); we shall have something to say later about actual methods of computation. Once we have the matrix of energy, we can set up the secular equation, and if we can solve it, we can set up the wave functions which form the best possible combinations of the original determinants, in order to approximate the true wave functions of the problem. We must remember that our formulas for matrix components have their rather simple form only on account of the orthogonality of the orbitals. If these were not orthogonal, the formulas would be exceedingly complicated, though even in that case they can of course be set up.

In most atomic problems we must solve a secular equation between a considerable number of determinantal wave functions, and this equation would be of very high order, and difficult to handle, if it were not for simplifying features. Thus if n' out of the n electrons have unpaired spins, we certainly are interested in all the states formed by choosing the spins of these electrons in either of the possible ways, so that we surely must consider $2^{n'}$ functions. Generally too there is orbital degeneracy as well as this spin degeneracy. The simplifying features arise from the conservation of angular momentum. If we disregard the magnetic spin-orbit coupling, both spin and orbital angular momentum are conserved, in the absence of an external field. We shall describe in the next section how this conservation can be used to help solve the problem. The first thing which we need to know, for this purpose, is how to find the matrix components of the various angular momentum vectors, between the various determinantal wave functions. We shall find that we wish the matrix components of the z component (where z is an arbitrary axis of space quantization) of spin angular momentum, and of the square of the magnitude of the spin angular momentum; and similarly for the orbital angular momentum. In finding these, we shall remember that the total angular momentum is the vector sum of the angular momenta of the various electrons. We start, then, by finding the matrix components of the x, y, and z components of angular momentum of a single electron, then by summing over all electrons, and finally, if we are interested in the square of the total angular momentum, in squaring the components and adding.

In finding matrix components of the angular momentum vectors, we are dealing with a problem which held a very important position in the development of quantum mechanics. The structure of multiplets, and particularly the Zeeman effect,(36) were problems which contributed very greatly to the vector model, and to the whole structure of quantum theory. For this reason, the interaction of angular momentum vectors was one of the first problems investigated by quantum mechanics. It was a problem for which the methods of matrix mechanics, introduced by Heisenberg(37) slightly before Schrödinger's wave mechanics, proved to be more convenient than the methods of wave me-

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[36] These problems are taken up in Sommerfeld's Atombau und Spektrallinien, previously mentioned. An excellent treatment, by two of the workers who contributed most to their understanding, is the book Zeemaneffekt und Multiplettstruktur der Spektrallinien, by E. Back and A. Landé, (Springer, Berlin) 1924. Many references to earlier work are given there.

[37] W. Heisenberg, Z. Physik 33, 879 (1925); M. Born, W. Heisenberg and P. Jordan, Z. Physik 35, 557 (1926); the theorems regarding angular momentum are well taken up in Elementare Quantenmechanik, by M. Born and P. Jordan, (Springer, Berlin) 1930. Many other writers during this same period contributed to the theory.

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chanics, proved to be more convenient than the methods of wave mechanics, though of course the two methods are intimately related.[38] The treatment of the electron spin, given in 1927 by Pauli,[39] was based on the general methods already worked out several years before, as if the electron were merely a spinning vector of angular momentum 1/2 unit. We shall use this point of view, referring the reader to QTM, pp. 479-485, and shall first set up the matrix components of the spin angular momentum of a single electron.

The starting point of the usual method of quantizing angular momentum is to assume that we have a set of wave functions differing from each other only in the component of angular momentum along the z direction, which is assumed to be quantized. If the quantum number representing the magnitude of the angular momentum is l, and the quantum number representing its component along the z axis is m, then, as shown in the references mentioned (see QTM, p. 482), the matrix components of angular momentum are the following:

$$\begin{aligned} M_x(m, m+1) &= M_x(m+1, m) = \sqrt{(l-m)(l+m+1)}\,(h/4\pi) \\ M_y(m, m+1) &= -M_y(m+1, m) = i\sqrt{(l-m)(l+m+1)}\,(h/4\pi) \qquad (1.8) \\ M_z(m, m) &= mh/2\pi. \end{aligned}$$

That is, M_x and M_y have components only between two wave functions whose quantum numbers m differ by one unit, while M_z has only diagonal components. We now apply these equations to the spin of a single electron, whose magnitude is $h/4\pi$, corresponding to $l = 1/2$, and for which therefore the quantum number m can take on only the two values $\pm 1/2$. We shall write the matrix components, not of the angular momentum itself, but of the angular momentum divided by $h/2\pi$, which we shall denote by the components s_x, s_y, s_z. Then we find, using (1.8), that the only components different from zero are

$$\begin{aligned} s_x(-1/2, 1/2) &= s_x(1/2, -1/2) = 1/2 \\ s_y(-1/2, 1/2) &= -s_y(1/2, -1/2) = i/2 \qquad (1.9) \\ s_z(1/2, 1/2) &= 1/2, \quad s_z(-1/2, -1/2) = -1/2. \end{aligned}$$

These vector components are half as large as those used by Pauli, in the reference just cited; he measured his angular momentum in units of $h/4\pi$ instead of $h/2\pi$ as we are doing.

We may now combine these expressions with our general method of finding matrix components of an operator, as given in Eqs. (1.5), (1.6), and (1.7), to find matrix components of the spin angular momentum, and of its square, with respect to the determinantal wave functions. The operators s_x, s_y, s_z are functions of spin only, and of a single electron only. Thus they are of the form f_i, mentioned earlier, and as pointed out before, there will be no non-diagonal matrix components between two states in which the quantum numbers of more than one electron change, and furthermore there will be no components between two states in which the orbital parts of the one electron functions change. If we denote the sum of the s_x's of all electrons by S_x, and similarly for the other components, we then find that S_x has non-vanishing components only between two states whose sets of orbitals u_i differ only in that one particular orbital for the initial state corresponds to the opposite spin from the same orbital for the final state; then the non-diagonal component of S_x equals 1/2. Similarly S_y has components only between such states, the non-diagonal component being $i/2$ if the spin changes from $-1/2$ to $+1/2$ going from the initial to the final state, but $-i/2$ if it changes from $+1/2$ to $-1/2$. The component S_z has only a diagonal matrix component, and this is composed out of contributions s_z from each electron. These contributions equal 1/2 for all electrons of + spin, $-1/2$ for all electrons of - spin. The sum of all these is the net z component of spin of all electrons, measured in units of $h/2\pi$; this is what is usually called M_S. Hence we see that S_z has a diagonal matrix, its diagonal component for any determinantal function being the M_S of that function.

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[38] The main points of this treatment are given in QTM, pp. 479-485.

[39] W. Pauli, Jr., Z. Physik **43**, 601 (1927).

We can now use these rules to find the matrix of $S_x^2 + S_y^2 + S_z^2$. To do this we need merely use the familiar rule for multiplication of two matrices. This means that the matrix of the product of two matrices F and G, between two states, equals the sum of products of matrix components of F from the initial state to all possible intermediate states, times the component of G from the intermediate state to the final state. In our calculation, then, we must look for all possible intermediate states between the initial and final state, and set up the appropriate products for each. We see at once that $S_x^2 + S_y^2 + S_z^2$ can have components only between two determinantal functions with the same orbital part of the one-electron functions, and that furthermore only two electrons can change their z component of spin in going from initial to final state: one in going from the initial to the intermediate state, another going from the intermediate to the final state. If both these electrons change their spin in the same direction (that is, if both go from + to -, or both from - to +), then the contributions of S_x^2 will be $(1/2)^2 = 1/4$, and of $S_y^2 (i/2)^2$ or $(-i/2)^2$, or $-1/4$, so that the contributions of $S_x^2 + S_y^2$ will cancel. If there are any changes of spin, the contribution of S_z^2 will be zero. Thus we see at once, by direct calculation, that $S_x^2 + S_y^2 + S_z^2$ will have non-vanishing matrix components only between two states of the same M_S, since if the spin of one electron changes from + to -, that of the other from - to +, the M_S will be the same in initial and final state.

Let us now calculate first the diagonal matrix component of $S_x^2 + S_y^2 + S_z^2$.

3. MATRIX COMPONENTS OF ENERGY AND ANGULAR MOMENTUM

From the operators S_x^2 and S_y^2, we shall have contributions from many intermediate states. In fact, if any one-electron function of coordinates appears in the determinantal function we are considering only once, with only one spin, we can have an intermediate state in which this electron appears with reversed spin. We can call such an electron an unpaired electron. For each such unpaired electron, then, the contribution of S_x^2 from the original state to this intermediate state with reversed spin, and then back to the initial state, will be 1/4. Similarly the contribution of S_y^2 will be 1/4; here, in contrast to the preceding case, the two factors multiplied together in finding S_y^2 will refer to transformations with the spin changing in opposite directions, so that we shall have $(i/2)(-i/2) = 1/4$, and the terms from S_y^2 will add to those from S_x^2 instead of subtracting. The net result, then, is that $S_x^2 + S_y^2$ will contribute an amount 1/2 to the diagonal component of the matrix, from each unpaired spin. Nothing will be contributed from paired spins, that is from orbital wave functions occupied by electrons of both spins, for then the intermediate state, in which one of the electrons changes the sign of its spin, would be forbidden by the exclusion principle. The operator S_z^2 will contribute simply M_S^2 to the diagonal component of the matrix. Thus we conclude that the diagonal component of $S_x^2 + S_y^2 + S_z^2$ with respect to a determinantal wave function equals the M_S^2 for that wave function, plus 1/2 times the number of electrons with unpaired spin in the wave function.

Next let us find the non-diagonal matrix components of $S_x^2 + S_y^2 + S_z^2$. There will be no contribution from S_z^2. We have already seen that there will be a component only if the spin of one orbital shifts from + to -, and of another orbital from - to +, in going from the initial to the final wave function. There will be two possible intermediate states: in one of them, the spin which was originally + has changed to -, but that which was originally - is unchanged, so that this is a state with two - spins for the orbitals in question; the other intermediate state is one with two + spins. In either case, S_x^2 contributes 1/4 going from the initial state through the intermediate state to the final one, and so does S_y^2, so that each intermediate state contributes 1/2 to the non-diagonal matrix component, and the two intermediate states together contribute unity. Each non-vanishing non-diagonal matrix component is then unity. We observe that any orbital function appearing twice in the determinant, once with + spin, once with -, will take no part in the non-diagonal matrix components, since the possible intermediate states formed from this would be forbidden by the exclusion principle.

We have seen, then, how to find the matrix components of $S_x^2 + S_y^2 + S_z^2$. We have followed in this the method introduced by Johnson,(40) who used these components in the way to be described in the next section. Johnson also computed, for reasons which we shall see shortly, the matrix components of $L_x^2 + L_y^2 + L_z^2$, where the L operator

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[40] M. J. Johnson, Jr., Phys. Rev. 39, 197 (1932).

stands for orbital angular momentum, divided by $h/2\pi$, just as the S stands for spin angular momentum. The procedure used in finding this is entirely analogous to what we have just shown. We start again with Eq. (1.8), but now the square roots do not simplify as they do with the spin. We find that L_x, L_y, L_z, the vector sum of the orbital angular momenta of all the electrons, have non-diagonal matrix components only between two states in which the orbital quantum number m of a single electron has changed by ± 1 unit, and these non-diagonal matrix components follow at once from Eq. (1.8). The quantity L_z has a diagonal matrix, the diagonal components being just M_L, the sum of the components of orbital angular momentum along the z axis for all electrons. We can find the matrix components of $L_x^2 + L_y^2 + L_z^2$ just as in the spin case, by matrix multiplication, though the formulas are not as simple as in the spin case. We find, as before, that there are no non-diagonal matrix components between two states of different M_L value. The only non-diagonal components then come between two states which differ in that the m of one electron has increased by 1 unit, and that of one other electron has decreased by 1 unit, between the initial and final functions. As for the spin, in calculating either diagonal or non-diagonal components, we must take account of all possible intermediate states, consistent with the exclusion principle, find the components of L_x^2 and L_y^2 arising from transitions from initial to final state through these intermediate states, using Eq. (1.8), and combine the results. The final result is very simple to work out, though the formula, as given in the reference cited by Johnson, is a little complicated to write down, simply because it tries to take account of all those cases permitted, or forbidden, by the exclusion principle. We shall not state the formulas, since the reader, if interested, can work them out for himself from the directions which we have given, about as easily as he can learn to understand the notation necessary to write them down explicitly.

Johnson also works out the matrix components of the scalar product $L_xS_x + L_yS_y + L_zS_z$, again for reasons which we shall explain shortly. Here again the method is obvious from what we have already said. This quantity has non-diagonal matrix components only between two states differing from each other in that the orbital angular momentum has had its component along the z axis decrease by 1 unit between the initial and final function while the z component of spin angular momentum has increased by an equal amount, or vice versa. The diagonal matrix component is simply M_LM_S.

4. Solution of the Secular Equation Problem for an Atom

We have already mentioned that in setting up the problem of the structure of an atom, we must use a considerable number of determinantal functions, to get a proper representation of the real wave functions describing the multiplets. It would be a difficult thing to solve the secular equation for the energy, between these determinantal functions, if we did not have additional information. This additional information is supplied by the behavior of the angular momentum, whose matrix components we have discussed in the preceding section. Let us now see how they are to be used. We shall first consider the case where the energy operator is just the Hamiltonian of Eq. (1.1), including only kinetic energy and electrostatic terms. Later we shall take up the more complicated case in which we consider also the magnetic interactions between spin and orbital motions of the electrons; these magnetic interactions, as we know, are responsible for the energy separation between the levels of the multiplets.

First we remind the reader of the simplified method of handling the problem introduced by the present writer[(41)] in his paper on the subject. We note in the first place that there are no non-diagonal matrix components of energy between states of different M_L or M_S values, so that we need to consider secular equations only between the various determinantal functions having a given M_L and M_S. This already greatly reduces the order of the secular equation. But further, we remember, as in the discussion just mentioned, that each energy value appears as a root of many of these secular equations. Thus when we wish to solve one of the secular equations, we may often find that all of its roots but one are already known. Then we may use the diagonal sum rule, according to which the sum of the diagonal matrix components of the energy matrix equals the sum of the roots of the secular equation, to find the one missing root by subtraction, and without having to solve the secular equation, or even to compute its non-diagonal components. By this means, as was shown in the reference quoted above, we can find the energy levels of all the multiplets, as far as they are determined by the electrostatic Hamiltonian of Eq. (1.1), provided we have only one multiplet of each L and S value. If we have more than one multiplet of a given L and S value, then the diagonal sum rule allows us only to find the sum of the energies of these multiplets. Thus, for instance, if we have the case of three non-equivalent s electrons, which can easily be shown to lead to a quartet and two doublets, the diagonal sum rule only leads to the sum of the energies of the two doublets.

For the cases where this method using the diagonal sum rule is applicable, it is the simplest way to solve the problem. However, there are several drawbacks connected with this method. In the first place, it is obviously inadequate if we have more than one multiplet of the same L and S value. In this case, we can still proceed. Suppose, for instance, that the diagonal sum rule allows us to find all but two of the roots of a secular equation of N rows and columns, giving only the sum of the two remaining roots. We can set up the whole secular equation, which we can do if we know the non-diagonal matrix components of energy. This will be an algebraic equation of the Nth degree, of which we know N-2 roots. If these roots are denoted by $E_1, \ldots E_{N-2}$, we know that the secular equation, which will be of the form of $E^N + A_1E^{N-1} + \ldots + A_N = 0$, must contain factors $(E - E_1)$, $(E - E_2)$, $\ldots (E - E_{N-2})$. We then divide the left side of the equation by these factors, and are automatically left with a quadratic, which we can solve by elementary methods. Extension of this method allows us in any case to take full advantage of the diagonal sum rule, and solve secular equations by numerical or other method only for the final inescapable problem of handling the various multiplets of the same L and S value. However, this procedure may be a little complicated, and

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[41] J. C. Slater, Phys. Rev. 34, 1293 (1929); taken up in QTM, pp. 158-198, 479-489.

we might wish a procedure for getting directly to the secular equation for these remaining multiplet energies. We know that the various solutions of the original secular equation correspond to multiplet states of various L and S values, and it would be a help if we could separate it out from the outset into equations each corresponding to only one particular L and one particular S value. This, as we shall see, can be done, and each one of these equations will then be reduced as far as is possible, from considerations of angular momentum.

The second drawback of the method of diagonal sums is that it does not yield the wave functions, but only the energy values, of the final states. These wave functions are often required. In particular, if we wish to include the magnetic interaction, which has been mentioned previously, the first step is ordinarily to solve for the degeneracy problem arising from the electrostatic interaction, then use the wave functions resulting from this as the starting point of a calculation of the energy levels and stationary states of the problem including magnetic energy. The first step is to compute matrix components of the magnetic interaction with respect to these wave functions, and this obviously cannot be done unless we know the wave functions. Here again a method of finding the wave functions associated with a definite value of L and S, as well as of M_L and M_S is needed.

Let us now see how a knowledge of the behavior of the orbital and spin angular momentum vectors can help us in our problem. We know (see QTM, as referred to) that the Hamiltonian operator H, of Eq. (1.1), commutes with the z components of orbital and spin angular momentum, and also with the squares of the magnitudes of these angular momenta, $L_x^2 + L_y^2 + L_z^2$ and $S_x^2 + S_y^2 + S_z^2$. Thus we can separately diagonalize all of these quantities, and in fact in the final wave functions, which we wish to arrive at, they are all diagonalized. The diagonal components of the z components of orbital and spin angular momentum are just M_L and M_S (in units of $h/2\pi$), and the diagonal components of $L_x^2 + L_y^2 + L_z^2$ and $S_x^2 + S_y^2 + S_z^2$ are $L(L + 1)$ and $S(S + 1)$ respectively, (see QTM, p. 482) where L and S are the orbital and spin quantum numbers. In addition, of course the energy is diagonalized in these final wave functions. In the original determinantal wave functions, the z components of orbital and spin angular momentum are diagonal, but the magnitudes are not, as we have seen in the preceding section, where we computed their non-diagonal matrix components, and of course the energy is not diagonal.

Now we remember that Schrödinger's equation $HU = EU$ is really a device for finding wave functions U with respect to which the energy is diagonalized. Similarly we could set up an operator equation, $(S_x^2 + S_y^2 + S_z^2)\,U = S(S + 1)U$, and if we solved it, the resulting function U would make the magnitude of the spin angular momentum diagonal. We can go further than in Schrödinger's equation, for we know in advance, by simple methods, that the diagonal matrix components equal $S(S + 1)$, so that we do not have to determine these quantities. It can now often be the case that this equation for the spin angular momentum can be solved more conveniently than Schrödinger's equation. For one thing, it does not depend on specific details of the energy operator, so that it can be solved once for all for large classes of problems. The resulting functions U will then have close relationships to the final solutions of Schrödinger's equation which we desire. There will, however, be widespread degeneracy in the solutions of this spin equation. We see, by analogy with Schrödinger's equation, that any two wave functions associated with the same S value, or same multiplicity, will act like degenerate states, and the equation will not uniquely determine the solutions, but only linear combinations of them. Thus we cannot hope to solve our whole problem by the use of these operators. But we can at least separate out the wave functions associated with the different multiplicites, and this is the sort of thing we are trying to do.

We can make our argument clearer by using one or two examples. Let us first take the familiar case of two non-equivalent s electrons, where we have a singlet and triplet. We know that we have four determinantal states: one, with $M_S = 1$, with two + spins: a second, with $M_S = 0$, with the first orbital function (which we may denote a) having a + spin, and the second (which we denote b) a - spin; a third, also with $M_S = 0$, with a having a - spin, b having a + spin; and a fourth state, with $M_S = -1$, with both - spins. From the rules for determining the matrix components of $S_x^2 + S_y^2 + S_z^2$, from the preceding section, we find at once that the first and fourth states have diagonal matrix components equal to 2, and no non-diagonal matrix components connecting them with any other state. This is as it should be; they both are connected with the triplet state, for which the diagonal components should be $S(S+1) = 2$. The states 2 and 3, with $M_S = 0$, have diagonal matrix components of unity, and non-diagonal matrix components also of unity. Let us now consider the resulting secular equation.

Let U_1, U_2 be the determinantal wave functions associated with these two states of $M_S = 0$, and let us write the linear combination which we are looking for $T_1U_1 + T_2U_2$. We wish to choose T_1, T_2 so that the equation $(S_x^2 + S_y^2 + S_z^2)(T_1U_1 + T_2U_2) = S(S+1)(T_1U_1 + T_2U_2)$ will be satisfied, where we are to insert $S = 0$ for the singlet, $S = 1$ for the triplet. In the usual way we multiply the equation above first by U_1^*, then by U_2^*, and in each case integrate over coordinates and sum over spin, and use the orthonormal properties of the U's. Then we have the matrix equations

$$\begin{aligned} \left[(S_x^2 + S_y^2 + S_z^2)_{11} - S(S+1)\right] T_1 + (S_x^2 + S_y^2 + S_z^2)_{12}\, T_2 &= 0 . \\ (S_x^2 + S_y^2 + S_z^2)_{12}\, T_1 + \left[(S_x^2 + S_y^2 + S_z^2)_{22} - S(S+1)\right] T_2 &= 0 . \end{aligned} \tag{1.10}$$

Here $(S_x^2 + S_y^2 + S_z^2)_{11}$ represents the (1, 1) matrix component of the square of the spin angular momentum, and so on. Putting in the known values of these matrix components, we have

$$\begin{aligned} \left[1 - S(S+1)\right] T_1 + T_2 &= 0 \\ T_1 + \left[1 - S(S+1)\right] T_2 &= 0 \end{aligned} \tag{1.11}$$

The secular equation associated with these two simultaneous linear equations is of course

$$\begin{vmatrix} 1 - S(S+1) & 1 \\ 1 & 1 - S(S+1) \end{vmatrix} = 0$$

whose solutions are at once found to be $S = 0, 1$, as we already knew they should be. If we put $S = 1$ in (1.11), to get the triplet wave functions, we find $T_1 = T_2$, so that the triplet wave function is the sum of the functions U_1 and U_2 (suitably normalized). Similarly putting $S = 0$ for the singlet, we find $T_1 = -T_2$. These results agree with those of elementary discussion (see QTM, p. 196), but we have obtained them without considering the form of the energy operator at all.

The case just considered is of course trivial; but now let us consider three non-equivalent s electrons, which is not trivial. Let the orbital parts of the wave functions be denoted by a, b, c. Then we have one determinantal function with $M_S = 3/2$, with + spins on all three orbitals; three determinantal functions with $M_S = 1/2$, of which one has + spins on a and b, a - spin on c, and the other two have the minus spins on a and b respectively; three similar functions with $M_S = -1/2$, and one with $M_S = -3/2$. We find at once that $(S_x^2 + S_y^2 + S_z^2)$ has a diagonal component of 15/4 for the states of $M_S = \pm 3/2$, and no non-diagonal components from these states to any others. These states correspond to the quartet, for which the diagonal component should be $(3/2)(5/2) = 15/4$, as is found. For the states with $M_S = 1/2$, we find diagonal components, all equal, of 7/4, and non-diagonal components between each pair, equal to 1. If we then set up a linear combination $T_1U_1 + T_2U_2 + T_3U_3$ of these functions, and proceed as before, the three equations analogous to (1.11) are

$$\begin{aligned} \left[7/4 - S(S+1)\right] T_1 + T_2 + T_3 &= 0 \\ T_1 + \left[7/4 - S(S+1)\right] T_2 + T_3 &= 0 \\ T_1 + T_2 + \left[7/4 - S(S+1)\right] T_3 &= 0 . \end{aligned} \tag{1.12}$$

We verify at once that the secular equation arising from these equations has a single root $S = 3/2$, and a double root $S = 1/2$, corresponding to the quartet and the two doublets. If we set $S = 3/2$ in Eq. (1.12), to get the T's corresponding to the quartet, we find

$$-2T_1 + T_2 + T_3 = 0, \quad T_1 - 2T_2 + T_3 = 0, \quad T_1 + T_2 - 2T_3 = 0$$

whose solution is at once found to be $T_1 = T_2 = T_3$. Thus the quartet function is the sum of U_1, U_2, and U_3, properly normalized. If on the other hand we set $S = 1/2$, to find the doublets, we find that all three equations reduce to one, $T_1 + T_2 + T_3 = 0$.

This single equation $T_1 + T_2 + T_3 = 0$ does not uniquely determine the wave functions of the two doublets, and we should not expect that it would. We can see what is happening better if we look at it geometrically. We remember that a wave function can be represented as a vector in a many-dimensional space. In our case, the three functions U_1, U_2, U_3 can be regarded as three orthogonal vectors in a three dimensional space. Then the combination

$T_1U_1 + T_2U_2 + T_3U_3$ is a vector in this space whose components along U_1, U_2, and U_3, which we may regard as unit vectors, are T_1, T_2, and T_3. The equation $T_1 = T_2 = T_3$, which holds for the quartet functions, means that this function is represented by a unit vector along the diagonal of the first octant, making equal angles with each of the axes. The other two vectors, representing the two doublets, must be orthogonal to this vector, or must lie in the plane normal to it. But we have found that these doublets are determined by the equation $T_1 + T_2 + T_3 = 0$, which, like the equation $x + y + z = 0$, is just the equation of this plane. We may choose any two unit vectors at right angles to each other in this plane, and they will then be suitable functions to represent the doublet functions. We may then find the matrix components of the Hamiltonian function with respect to these two functions, and solve the resulting quadratic secular equation, yielding the two doublet energy levels and wave functions of the problem. Thus we have avoided having to solve a cubic secular equation between all three states with $M_S = 1/2$.

In order to set up the secular equation between these two doublet states, we must find the matrix components of energy with respect to these wave functions of the form $T_1U_1 + T_2U_2 + T_3U_3$, when we know the matrix components with respect to the U's. This is a straightforward problem in the transformation theory of matrix mechanics: the problem of finding the matrix components of any operator with respect to the transformed wave functions $\sum(j)\ T_{ij}U_j$, when we know the matrix components of the operator, which we may take to be H_{ij}, with respect to the original functions U. This transformation theory was worked out in the beginning of the development of matrix mechanics, appearing in the original papers of Heisenberg and others, already cited. It is thus a familiar theory; but since it is not taken up in QTM, it may not be familiar to the reader, and for that reason we show how to carry out the transformation. The matrix component of an operator like H, with respect to the original functions U, is defined as $H_{ij} = \int U_i^* HU_j\, dv$. To find the matrix components, which we shall define as H_{ij}', with respect to the transformed wave functions, we obviously have

$$\begin{aligned} H_{ij}' &= \int \Big(\sum(k)\ T_{ik}^*\ U_k^*\Big)\ H\ \Big(\sum(n)\ T_{jn}U_n\Big)dv \\ &= \sum(k,n)\ T_{ik}^*\ H_{kn}\ T_{jn} \end{aligned} \qquad (1.13)$$

This simple formula contains enough of the transformation theory for our present purposes, or for most purposes. The T's are determined by our discussion of the spin operator, as mentioned above, the matrix components H_{kn} are computed by the usual rules with respect to the original determinantal wave functions, and Eq. (1.13) allows us at once to set up the matrix components H_{ij}' with respect to our combinations of determinants, set up to diagonalize the magnitude of the angular momentum. Thus we have all the necessary ingredients for making use of the spin in the process of solving our secular equation, in the problem of a complex spectrum.

We have seen how we can help solve the secular equation by use of spin angular momentum. In the example we chose, of three non-equivalent s electrons, there is of course no orbital angular momentum, so that we can make no use of it. But in cases where there is orbital angular momentum, the diagonalization of the spin will not accomplish all that is possible before we write the secular equation. In such a case, among the solutions corresponding to a given M_L and M_S, we have solutions corresponding to different spins S, and also to different azimuthal quantum numbers L. By diagonalizing $S_x^2 + S_y^2 + S_z^2$, we shall be left with a degeneracy between the states corresponding to different L's. We can then carry out the same process over again, but now applied to orbital angular momentum. That is, we can take the transformed wave functions corresponding to a given value of M_S, M_L, and S, and tranform the operator $L_x^2 + L_y^2 + L_z^2$ to this set of wave functions, using the type of transformation given in Eq. (1.13). Then we set up a secular equation for diagonalizing this quantity, just as we did earlier for the spin. This will allow us to find new wave functions, combinations of the ones found before, which make both the magnitude of the spin and of the orbital angular momentum diagonal. The energy operator will have no non-diagonal matrix components between the states of different S and L, so that if we transform the energy operator to these functions, we shall be in position to set up the secular equation for the energy.

This is as far as we need to carry the problem, if we are considering only electrostatic energy. If we are including also the magnetic interaction terms, however, we must go further. We shall not discuss the nature of these terms in the Hamiltonian in detail at present, but for our present purposes we need only note that they take the form of torques between the orbital and spin angular momenta of the various electrons, torques internal to the system, so that they allow the total angular momentum of the whole atom to be conserved, but destroy the conservation of the orbital and spin angular momenta separately. In other words, once these terms are included in the Hamiltonian, the quantities measured by M_S, M_L, S, and L are no longer constants of the motion, but J, which represents the magnitude of the vector sum of orbital and spin angular momentum, and M_J, its component along the axis, will still be conserved. In other words, the total Hamiltonian still commutes with the operators represented by $S_z + L_z$, and by $J_x^2 + J_y^2 + J_z^2 = (S_x + L_x)^2 + (S_y + L_y)^2 + S_z + L_z)^2$, which in turn equals $(S_x^2 + S_y^2 + S_z^2) + (L_x^2 + L_y^2 + L_z^2) + 2(S_xL_x + S_yL_y + S_zL_z)$. Let us then diagonalize this quantity. Since $S_x^2 + S_y^2 + S_z^2$ and $L_x^2 + L_y^2 + L_z^2$ have already been diagonalized, and since both these quantities can be easily proved to commute with $S_xL_x + S_yL_y + S_zL_z$, we can diagonalize the latter quantity without destroying the diagonalization of the magnitude of spin and orbital angular momentum (though this diagonalization will be destroyed when we diagonalize the magnetic interaction in the Hamiltonian). Since we have noted that $S_xL_x + S_yL_y + S_zL_z$ involves non-diagonal components between terms with different M_S and M_L, but the same M_J, we shall find that this diagonalization, which we can carry out by the same procedure as previously, will lead to final wave functions which are combinations of several of our earlier functions, all corresponding to the same S and L values, but with different M_S and M_L though the same M_J.

4. SOLUTIONS OF THE SECULAR EQUATION PROBLEM FOR AN ATOM

Each of the final wave functions which we have obtained in this way corresponds to a definite S, L, J, and M_J. The matrix of the electrostatic part of the Hamiltonian is diagonal with respect to these wave functions, as far as non-diagonal components between different S and L values are concerned. Let us assume that we have solved the resulting secular equations for the electrostatic energy, so that we have completely diagonalized the electrostatic energy. We have then secured the correct wave functions to describe the L-S or Russell-Saunders coupling, in which we assume the magnetic interaction to be negligible compared to the electrostatic terms. Next we set up the matrix components of the magnetic energy. This can easily be done (though we have not shown how to do it) in the original determinantal wave functions. We have found the complete transformation from these functions to our final functions expressing L-S coupling, with J diagonalized. We find that we have non-diagonal matrix components of this magnetic energy only between functions with the same J value, as we see from the fact that the complete energy operator commutes with $J_x^2 + J_y^2 + J_z^2$, but there are non-diagonal matrix components between states with different S and L values, since in the presence of the magnetic torques the spin and orbital angular momenta are no longer constants of the motion. In case these non-diagonal components are small compared to the energy separation between the multiplets, we have the case of Russell-Saunders coupling. In that case, for a first approximation, we can disregard these non-diagonal matrix components. The diagonal matrix components of the magnetic energy will then give the correct multiplet separations, and from the form of the magnetic energy we derive the Landé interval rule, and other properties of the multiplets mentioned in the references already given.

If the non-diagonal matrix components of magnetic energy between different multiplets are not negligible, however, we must solve a secular equation between all states of the same J value, and there is no way of further simplifying this secular equation, though we know its matrix components. The result will be a deviation of the multiplet separations from the Landé interval rule, and from Russell-Saunders coupling. In the extreme case where the magnetic energy is large compared to the electrostatic terms, which can occur in some cases with heavy atoms, the departure from Russell-Saunders coupling can be complete, and we can have what is called j-j coupling. We do not have to do anything different to solve our problem, however; the solution of the secular equation between all states of the same J value will still give the final energy levels of the problem.

The only remaining complication which is ordinarily introduced is to impose an external magnetic field, resulting in the Zeeman effect. It is easy to find the matrix components of this external magnetic energy in the original, determinantal wave functions. But by the various steps which we have outlined, we now know the complete transformation from these original determinantal functions to the final functions, taking account of electrostatic energy and of the magnetic interactions within the atom. In the presence of an external magnetic field, J is no longer a constant of the motion, only M_J being constant. Thus we have non-diagonal matrix components of the external magnetic energy between states of the same M_J but different J. If the magnetic field is small, these non-diagonal matrix components can be neglected. If it is large, however, they must be considered, and we must solve a final secular equation between all states of the same M_J. In the case where we neglect the non-diagonal matrix components, we have the ordinary Zeeman effect; if we have to consider them, we have the Paschen-Back effect, which occurs when the Zeeman splitting is comparable with the separation between multiplet levels in the absence of the magnetic field. The procedure we have outlined, in principle, allows us to find this Paschen-Back effect in all intermediate cases between Russell-Saunders and j-j coupling.

We have outlined in this section the general treatment of the secular equation for the problem of a complex spectrum, including all the types of simplification which can be deduced from the angular momentum relations. With this treatment, a certain part of the theory of complex spectra is really complete, though of course we have not worked out detailed examples. The theory was worked out by a number of persons, in the years immediately following the development of the determinantal method in 1929. Among them we may particularly mention E. U. Condon and G. H. Shortley, as well as M. H. Johnson, Jr., to whom we have already referred. The well-known text by Condon and Shortley summarizes most of this work, though the original papers are often easier to read than the text. We give below a bibliography of some of the principal papers dealing with the determinantal method as applied to complex spectra, mostly in the period from 1929 to 1935, when Condon and Shortley's *Theory of Atomic Spectra* (Cambridge) was published.

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5. The Hartree-Fock Method

In the preceding sections, we have been handling principally one aspect of the determinantal method for atoms: the solution of the secular equation between a number of different determinantal functions, made up out of one-electron orbitals. Now we turn to the other aspect of the problem, the choice of one-electron orbitals. First we consider the case where we are dealing with only a single determinantal function; in this case we are led to the Hartree-Fock method.

In Section 1, we have mentioned that Hartree arrived at his self-consistent field method in an intuitive manner. It occurred independently, however, to the present writer(42) and to Fock,(43) that it ought to be possible to derive Hartree's equations in a straightforward manner from the variation principle of quantum mechanics. If H is the Hamiltonian operator for a given problem in quantum mechanics, and if u is a normalized, but otherwise arbitrary function of the coordinates and spins of the particles of the problem, then we may construct the diagonal energy $\int u^* H u \, dv$. This will have a definite value for each value of the function u. Then we can show that if u is one of the correct wave functions of the problem, this energy integral is stationary with respect to small variations of the wave function. That is, if u departs from one of the correct wave functions by a small quantity of the first order, the diagonal energy will depart by a small quantity of the second order. This result, which seems very plausible from the known behavior of the perturbation theory of quantum mechanics, is easy to prove, and we shall give a proof presently, in case the reader is not familiar with it. In particular, if we are dealing with the lowest stationary state of the problem, the diagonal energy takes on a minimum value for the correct wave function of the problem: no incorrect wave function u can give as low a value for the energy integral as the correct wave function.

If now we have a function with a number of parameters in it, we can get a certain amount of variation into the function by varying the values of these parameters. If we compute the energy integral $\int u^* H u \, dv$ as a function of these parameters, we may reasonably hope that if we choose those values of the parameters that make the energy integral a minimum, we shall obtain the best approximation to the ground state of the system which the given function is able to take on, by variation of its parameters. There is one particularly simple case of this method. That is the one in which the assumed function is a linear combination of a number of given functions, so that the coefficients in this linear combination are the parameters in question. Then it proves to be true, and we shall prove it shortly, that the result of the variation method is just the same as the result of the ordinary perturbation method, which also deals with a sum of a number of unperturbed functions. But the variation method is much broader than this, for the parameters can enter into the function in any arbitrary way, and still we can vary these parameters to make the energy integral a minimum. For instance, we

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[42] J. C. Slater, Phys. Rev. 35, 210 (1930).

[43] V. Fock, Z. Physik 61, 126 (1930).

may have a wave function whose general shape is known to be correct, but whose scale is not fixed: we might use a more extended or more concentrated wave function. We can compute the energy as a function of the scale factor, vary this to make the energy a minimum, and thus get the best approximation to the wave function of the ground state. We shall mention such applications later.

The application of the variation principle leading to the Hartree method is a broader one, however. Suppose we approximate the wave function of the n-electron problem by the product of one-electron functions $u_1(x_1s_1) \ldots u_n(x_ns_n)$. We can compute the energy integral for this function. We can then ask what one-electron functions $u_1 \ldots u_n$ will make the energy integral a minimum. This question can be formulated mathematically, and it leads to partial differential equations for the functions $u_1 \ldots u_n$, which, with very minor qualifications, are the differential equations to which Hartree had already been led intuitively. If instead of the simple product of one-electron functions we take the determinantal function of Eq. (1.2), so as to take proper account of the antisymmetry of the wave function, we can again compute the energy integral, and can again vary the one-electron orbitals to make the energy a minimum. This leads to slightly different equations, and these are generally called the Hartree-Fock equations. These equations, then, give the best one-electron orbitals to use in constructing a single determinantal approximation to the true wave function of the ground state of a system. We shall now go through the problem of setting up these equations in detail, [illegible] shall then investigate their nature and meaning.

First, we consider the variation method itself. It is well known that very generally the differential equations of the type of Schrödinger's equation can be derived from variation principles; the reader acquainted with the general theory of the Sturm-Liouville equation will be familiar with this fact. Schrödinger, in his first paper setting up wave mechanics, set up a variation principle from which he derived his equation. The integral which he used is slightly different from the integral $\int u^* H u \, dv$ which we are considering: in place of the Laplacian operator to represent the kinetic energy, the square of a gradient appears. Schrödinger's form is the correct and more general way to write the variation principle, but the form which we have described can be derived from it in a great many cases, and is satisfactory for most ordinary applications (the exceptions come where there are surfaces over which the function u has a discontinuous slope). We do not wish here to give a general discussion of variation principles, but shall merely give a simplified discussion of the principle as applied to Schrödinger's equation, sufficient for our present purposes.

Let us consider the energy integral $\int u^* H u \, dv$, and let us make a small change in u, so that it changes to $u + \delta u$, where δu, like u, is a function of the coordinates and spin. Of course, we must make a corresponding change δu^* in u^*. Then the change produced in the energy integral is $\int \delta u^* H u \, dv + \int u^* H \, \delta u \, dv$. We wish to have this change a small quantity of higher order, provided u remains normalized. This proviso can be stated by saying that the normalization integral $\int u^* u \, dv$ is to be unchanged, or that its change, which we may write as $\int \delta u^* u \, dv + \int u^* \delta u \, dv$, is zero. We shall first show that the second term in each of these expressions is merely the complex conjugate of the first. This is obvious with the normalization integral, where the second term may be written as $\int \delta u \, u^* \, dv$. With the energy integral, it is also obvious with the potential energy term. Thus let the potential energy operator be V. Then the second term in the variation of the potential energy integral is $\int u^* V \delta u \, dv$, which is the conjugate of $\int \delta u^* V u \, dv$, since V is always real.

With the kinetic energy integral, we must use Green's theorem. Thus if we had a problem with only one particle, H would involve the operator ∇^2. Now by Green's theorem,

$$\int (u^* \nabla^2 \delta u - \delta u \nabla^2 u^*) \, dv = \int (u^* \operatorname{grad} \delta u \cdot n - \delta u \operatorname{grad} u^* \cdot n) \, da ,$$

where the right-hand side represents a surface integral over the surface bounding the volume of integration, and n represents the outer normal. In the ordinary cases, with Schrödinger's equation, the integration can be over all space, and the surface integral vanishes. Thus we see that the kinetic energy term in $\int u^* H \delta u \, dv$ is the conjugate of that in $\int \delta u^* H u \, dv$. Our proof applies directly only with one particle, but the extension to many particles is very simple, using a many-dimensional form of Green's theorem. We thus have shown that the second integral in both of our expressions is the conjugate of the first. If, then, we can demand that the variation $\int \delta u^* H u \, dv$ be a small quantity of higher order, for all variations δu^* for which the variation $\int \delta u^* u \, dv$ is zero, we shall have proved our point, for the complex conjugate of $\int \delta u^* H u \, dv$ will also be small of higher order, and the complex conjugate of $\int \delta u^* u \, dv$ will also be zero. The result is just as if we varied only u*, leaving u unchanged.

In the preceding paragraph, we have merely asked how to state the condition that the energy integral be stationary for all changes of u which leave u normalized; we have not yet asked what results from this condition. As a step in asking this question, we use the method of undetermined multipliers, which is generally used when we have a variation problem with a subsidiary condition, such as our normalization condition. If it were not for this subsidiary condition, we could state the consequences of having the energy integral stationary at once. If the integral $\int \delta u^* H u \, dv$ is to be a small quantity of higher order, independent of δu^*, we must clearly have H u everywhere zero, for if it were different from zero for any value of the coordinates, we could let δu^* be different from zero only in that neighborhood, and we should certainly find that the integral was not zero. This is the usual procedure used in the calculus of variations. But when we have a subsidiary condition, we demand not that H u be everywhere zero, but only that a linear combination of H u and of u, the quantity appearing in the other integral $\int \delta u^* u \, dv$, be everywhere zero. Let us write this linear combination $Hu - Eu$, where E is a constant (which we shall shortly connect with the ordinary energy of the Schrödinger problem). If now we demand that $Hu - Eu = 0$, then we shall have $\int \delta u^* H u \, dv = E \int \delta u^* u \, dv$, so that $\int \delta u^* H u \, dv$ will clearly be zero for any variation δu^* for which $\int \delta u^* u \, dv = 0$, just as we desire. But $Hu - Eu = 0$ is just Schrödinger's equation, where now E evidently is the ordinary energy appearing in that equation. Thus we show that the condition that the energy integral $\int \delta u^* H u \, dv$ be stationary, for any variation δu which leaves u normalized, is that u satisfy Schrödinger's equation. This is the theorem which we wished to prove. Of course the energy integral will differ by small quantities of higher order from its stationary value, and with some types of variation of U it may increase, with other types of variation it may decrease. This is like the behavior of a function of several variables, at a point where it is stationary. Generally this point is what is called a saddle point, and not a true maximum or minimum. But clearly for the ground state of the system, which by definition has the lowest energy level, the energy integral cannot decrease with any type of variation of u, for if it did, we should eventually come to a still lower stationary value, and a lower eigenvalue, which would contradict the postulate that we were dealing with the ground state.

The arguments which we have given are not presented with mathematical rigor, but the rigorous proofs can be given, and lead to the same results which we have stated. Let us now see first how the variation method leads at once to the ordinary secular equations of perturbation theory. Suppose we have a set of orthogonal functions $u_1 \ldots u_n$, and that we try to express u as a linear combination $\sum(i)\, C_i u_i$ of these functions. We ask what combinations best represent true solutions of Schrödinger's equation. The integral $\int u^*(H - E)\, u\, dv$ equals $\sum(i, j)\, C_i^* C_j \int u_i^*\, (H - E)\, u_j\, dv$. We have seen that if we set the variation of this integral equal to zero, when only u* varies, we shall obtain our desired condition. In particular, let us vary u by allowing only one of the C_i^*'s to vary; in effect, we set the partial derivative of the integral with respect to C_i^* equal to zero, not varying the C_j's. Then, remembering the definition of the matrix components H_{ij} of the energy operator with respect to the functions u_i, and remembering their orthogonality, the equations resulting are $\sum(j)\, C_j(H_{ij} - E\delta_{ij}) = 0$. But these are just the ordinary equations resulting from the perturbation method (see for instance QTM, Eq. (4. 1. 3)). Thus specifically we show that the best way to combine a finite set of orthogonal functions to get a linear combination representing the true solution of Schrödinger's equation is by setting up these ordinary equations between them, following the pattern of the perturbation theory, and resulting in a secular equation for the energy.

Now we are familiar enough with the variation method to proceed to our problem of the Hartree-Fock equations. We are required to set up a single determinant of one-electron orbitals; to compute the diagonal matrix component of H with respect to this determinant; and to ask how this diagonal matrix component varies when any one of the one-electron orbitals is varied in an arbitrary manner, subject only to the condition that this one-electron orbital remain normalized, and orthogonal to each of the other orbitals. The resulting variation must be a small quantity of a higher order, when any one of the orbitals is varied. We may use (Eqs. (1. 1) and (1. 5) to compute the required matrix component. Setting up the problem of a single atom of nuclear charge Z units, the integral $\int u^*\, H\, u\, dv$ is

$$\begin{aligned} &\sum(i) \int u_i^*(x_1)(-\nabla_1^2 - 2Z/r_1)\, u_i(x_1)\, dv_1 \\ &+ \sum(\text{pairs } i, j) \int u_i^*(x_1)\, u_j^*(x_2)(2/r_{12})\, u_i(x_1)\, u_j(x_2)\, dv_1 dv_2 \\ &- \sum(\text{pairs } i, j;\ \text{spin } j = \text{spin } i) \int u_i^*(x_1)\, u_j^*(x_2)(2/r_{12})\, u_j(x_1)\, u_i(x_2)\, dv_1 dv_2 \,. \end{aligned}$$

We now vary one of the u*'s, say u_i*. The resulting varied integral is

$$\begin{aligned}&\int \delta u_i*(x_1)(-\nabla_1^2 - 2Z/r_1)\, u_i(x_1)\, dv_1 \\ &+ \sum(j \neq i) \int \delta u_i*(x_1)\, u_j*(x_2)(2/r_{12})\, u_i(x_1)\, u_j(x_2)\, dv_1 dv_2 \\ &- \sum(j \neq i;\ \text{spin } j = \text{spin } i) \int \delta u_i*(x_1)\, u_j*(x_2)(2/r_{12})\, u_j(x_1)\, u_i(x_2)\, dv_1 dv_2 \ .\end{aligned}$$

Now we wish to make this variation zero, for all variations δu_i* which leave u_i* normalized, or which have $\int \delta u_i* u_i\, dv = 0$, and which leave it orthogonal to all other u's, or which have $\int u_i* u_j\, dv = 0$, or $\int \delta u_i* u_j\, dv = 0$. By the method of undertermined multipliers, we may set a linear combination of all the various varied integrals equal to zero. That is, we may write our condition

$$\begin{aligned}&(-\nabla_1^2 - 2Z/r_1)\, u_i(x_1) \\ &+ \sum(j \neq i) \left[\int u_j*(x_2)(2/r_{12})\, u_j(x_2)\, dv_2\right] u_i(x_1) \\ &- \sum(j \neq i;\ \text{spin } j = \text{spin } i) \left[\int u_j*(x_2)(2/r_{12})\, u_i(x_2)\, dv_2\right] u_j(x_1) \\ &= \sum(j)\, \lambda_{ij}\, u_j(x_1) \ .\end{aligned} \tag{1.14}$$

The equations (1.14) are the Hartree-Fock equations for the orbitals $u_i(x)$. We shall now go on to discuss their significance.

6. Significance of the Hartree-Fock Equations

Before we take up the general Hartree-Fock equations, let us examine the simplified form which they take when we use only a product of orbitals as a wave function, rather than the determinantal function. In this case, the last term on the left side of Eq. (1.14) is missing, for this term, if we examine the derivation of Eq. (1.5), comes from interchanges of orbitals which occur only with the determinantal function. Furthermore, there is no requirement in this case that the one-electron orbitals be orthogonal, so that only the term for i = j on the right side of Eq. (1.14) is present. Thus we have the simplified equation

$$\begin{aligned}&(-\nabla_1^2 - 2Z/r_1)\, u_i(x_1) \\ &+ \sum(j \neq i)\left[\int u_j*(x_2)(2/r_{12})\, u_j(x_2)\, dv_2\right] u_i(x_1) \\ &= \epsilon_i\, u_i(x_1) \ ,\end{aligned} \tag{1.15}$$

where we have used ϵ_i in place of λ_{ii}. This equation has a very simple meaning. The quantity $\sum(j \neq i) \int u_j*(x_2)(2/r_{12})\, u_j(x_2)\, dv_2$ is simply the electrostatic potential, at point x_1, of the charge distributions $u_j* u_j$ of all other electrons. In other words, Eq. (1.15) states that u_i is the solution of an ordinary Schrödinger equation for the motion of an electron in the field of the nucleus, and of all the other electrons distributed according to the wave functions u_j. The energy ϵ_i is the one-electron energy of this problem. But this condition, with a trifling reservation, is just that to which Hartree was led by intuitive reasoning, and which he made the basis of his calculation. The trifling exception is that the potential as determined from the charge distributions of all other electrons is not generally spherically symmetrical, and Hartree used the average of this potential over all directions, to get a spherical potential, so as to be able to carry out the solution of Schrödinger's equation. We thus see how Hartree's method really gives the best one-electron orbitals, provided we use a product of such orbitals as a many-electron wave function.

Now let us ask what is the physical meaning of the additional complications present in Eq. (1.14). In the first place, we can show that the right side of Eq. (1.14) can be simplified: we can always choose solutions u_i so that the quantity λ_{ij} forms a diagonal matrix, and the right side of (1.14) can be rewritten as $\epsilon_i u_i(x_1)$, just as we have written it in (1.15). We shall not give the complete proof of this statement, but can easily give the physical reason behind it. It is a characteristic of a determinantal function, like that of Eq. (1.2), that we can make up a new determinant out of it, by setting up new orbitals $u_1' \ldots u_n'$ which are formed from $u_1 \ldots u_n$ by a unitary transformation, and the new determinant will have a value identical with the original determinant. It is obvious, then, that our variation method, which makes statements only about the determinant as a whole, cannot uniquely determine the u_i's. Any set of orbitals determined from them by a unitary transformation must equally well satisfy the variation principle, and hence the Hartree-Fock equations. But we can investigate the behavior of the matrix λ_{ij} when we make such a unitary transformation, and we find that it transforms just like ordinary matrices. It is possible, then, to find a unitary transformation of the u_i's which makes this matrix diagonal. We do not lose in generality, then, if we assume from the beginning that it is diagonal, and for most purposes this is a desirable feature. We shall then assume it in our further work.

The resulting Hartree-Fock equation has been the subject of a good deal of discussion, and has been made the basis of considerable calculation. Among those contributing to its understanding were Dirac,$^{(44)}$ Brillouin,$^{(45)}$ and Hartree.$^{(46)}$ The original formulation of Fock was not so straightforward in the matter of the interpretation of the spin as the derivation we have given, which resembles more those of the writers just quoted. Hartree and others have made numerical calculations, using Eq. (1.14), for a number of atoms, and the results differ significantly from those of the original Hartree equations. By now, calculations have been made for a good many atoms, by one or the other of the methods.$^{(47)}$ The quantities forming the

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[44] P. A. M. Dirac, Proc. Cambridge Phil. Soc. 26, 376 (1930).

[45] L. Brillouin, Les Champs Self-Consistents de Hartree et de Fock, Actualites Scientifiques et Industrielles No. 159 (Hermann et Cie., Paris, 1934)

[46] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) A150, 9 (1935)

[47] For a very complete listing of the atoms which have been investigated by this method, with references to the literature, see the 1951 edition of Landolt-Bornstein, Physikalisch-chemische Tabellen.

last term on the left side of Eq. (1.14), however, have been regarded as fairly mysterious and difficult to interpret in a physical way. The present writer[48] has recently discussed these terms, in such a way as to make their physical meaning clear.

In the first place, we note that in the second and third terms of Eq. (1.14), we can add and subtract terms for $j = i$, without making any change in the equation. In the third term, we can also multiply and divide by $u_i^*(x_1)\, u_i(x_1)$. When we make these changes, Eq. (1.14) takes on the following form:

$$\begin{aligned} &(-\nabla_1^{\,2} - 2Z/r_1)\, u_i(x_1) \\ &+ \sum(j) \left[\int u_j^*(x_2)(2/r_{12})\, u_j(x_2)\, dv_2 \right] u_i(x_1) \\ &- \left[\frac{\sum(j\colon \text{spin } j = \text{spin } i) \int u_i^*(x_1)\, u_j^*(x_2)(2/r_{12})\, u_j(x_1)\, u_i(x_2)\, dv_2}{u_i^*(x_1)\, u_i(x_1)} \right] u_i(x_1) \\ &= \epsilon_i\, u_i(x_1)\ . \end{aligned} \tag{1.16}$$

The revised form (1.16) of the Hartree-Fock equation shows that u_i is the solution of a Schrödinger equation with a Hamiltonian operator which is the sum of the kinetic energy, the potential energy in the field of the nucleus, the potential energy in the field of all electrons (including the electron whose wave function we are finding), and a correction term, the last on the left of Eq. (1.16), involving exchange integrals. It is this last term which we wish to interpret. Since we can be quite sure that the electron does not really exert a Coulomb interaction in itself, it is clear that somehow this last term must correct for the interaction of the particle with itself, which is erroneously included in the second term of Eq. (1.16). We may regard this last term on the left side of Eq. (1.16) as representing the potential, at the position x_1 of the electron in question, of a charge distribution at point x_2, of magnitude

$$- \sum(j\colon \text{spin } j = \text{spin } i)\ \frac{u_i^*(x_1)\, u_j^*(x_2)\, u_j(x_1)\, u_i(x_2)}{u_i^*(x_1)\, u_i(x_1)} \tag{1.17}$$

Since this charge density is connected with the exchange term in Eq. (1.16), we may call it the exchange charge density.

We can easily prove two properties of the exchange charge density. First, its total amount is one electronic charge (which equals -1 in atomic units). To prove this, we integrate over dx_2. We use the orthogonality of the u_i and u_j's (which we shall prove shortly), to show that all terms in the summation (1.17) go out on integration, except for $j = i$, and this term integrates to unity. Secondly, at the point $x_2 = x_1$, the summation (1.17) reduces to $-\sum$(j: spin j = spin i) $u_j^*(x_1)\, u_j(x_1)$, or the total density of all electrons of the same spin as the ith, at the position x_1. These two properties will allow us to deduce the general nature of the exchange charge density, and its physical significance.

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[48] J. C. Slater, Phys. Rev. 81, 385 (1951)

The potential energy of the field in which the electron moves, as given by the Hartree-Fock equation in the form (1.16), is that arising from the nuclei; from all electrons of spin opposite to that of the electron considered, as determined from the wave functions of those electrons of opposite spin; but from a charge distribution of electrons of the same spin equal to the total charge of these electrons, corrected for the exchange charge density. That is, this charge distribution of electrons of the same spin adds up to one less than the total number of electrons of this spin, or it includes all electrons of this spin with the exception of the one whose wave equation we are considering. This is obviously as it should be. The net charge density of electrons of this spin, corrected for the exchange charge, goes to zero at the point x_1 where the electron is located, for we have seen that at $x_2 = x_1$, the exchange charge density just cancels the total density of all electrons of this spin. This is as if the electron whose wave function we were finding carried around with it a hole, centered on its position x_1, such that electronic charge of total amount one unit were removed from the immediate neighborhood of its position. In other words, we may say that in the Hartree-Fock method each electron moves in the field of the nuclei, of all electrons of opposite spin, but in the field of a charge distribution of electrons of the same spin equal to the total charge distribution of such electrons, diminished by a single electronic charge which is removed from this hole surrounding the position of the electron. This hole is clearly a result, in a way, of the exclusion principle, which keeps other electrons of the same spin away from it. For this reason, on account of the close connection of the exclusion principle with the Fermi statistics, it is often referred to as the Fermi hole. Since the exchange charge density (1.17) has a different form for each wave function u_i, we clearly have a different potential for each of these wave functions. The total exchange charge, however, equals one electronic charge in each case, and its value when $x_2 = x_1$ is in each case equal, so that the net size of the Fermi hole must be approximately the same for each wave function, even though it may differ in shape and other details. Thus we may commit no very great error if we replace the actual Fermi holes, which are different for each u_i, by an averaged value taken to be the same for all u_i's. We shall discuss this possibility in a later section, after taking up some of the properties of solutions of the Hartree-Fock equations.

7. Properties of Solutions of the Hartree-Fock Equations

Before we go further in discussing the Hartree-Fock equations, we shall prove two properties of their solutions. First, we shall prove that the one-electron orbitals u_i derived from them are orthogonal. We have really assumed this orthogonality in setting up the equations themselves, but it does not seem intuitively obvious, from Eq. (1.16), since as we have just seen each orbital is a solution of a Schrödinger equation for a different potential. To prove the orthogonality, we proceed as always in Schrödinger's equation. We set up Eq. (1.16) for u_i, and multiply by $u_k^*(x_1)$. Then we set up the Hartree-Fock equation, like (1.16), for $u_k^*(x_1)$, replacing i by k, and taking the conjugate, and multiply this by $u_i(x_1)$. We then subtract one of these quantities from the other, and integrate over the coordinate dv_1. Really, we should include the spin along with the coordinates in Eq. (1.16), and sum over spin as well as integrating over coordinates, in each case. On the right side, then, we shall have $(\epsilon_i - \epsilon_k) \int u_k^*(x_1)\, u_i(x_1)\, dv_1$. On the left side, most of the terms will automatically cancel, just as in the conventional case of Schrödinger's equation. Thus we get rid of the Laplacian terms by integration by parts in the familiar way, and the potential energy terms in the field of the nucleus, and in the field of all other electrons, automatically cancel. The only term which could give trouble is the exchange charge term. But when we write this out, we find that it cancels too, so that we are left with the statement $(\epsilon_i - \epsilon_k) \int u_k^*(x_1)\, u_i(x_1)\, dv_1 = 0$, which leads to orthogonality just as in a conventional Schrödinger's equation. We note that this is only on account of the special form of the exchange charge density. The same proof does not apply, as we can readily verify, for solutions of the ordinary Hartree equations. Those solutions, in fact, are not orthogonal, and this is one of the great advantages of the Hartree-Fock over the Hartree equations, since it is so important to have orthogonal orbitals when using the determinantal method. We notice another fact also, if we examine the proof carefully. This is that the orthogonality of two orbitals connected with different spins comes from the summation over the spin coordinates (which we have not written down explicitly, but which should be there), rather than from the integration over the space coordinates. It does not necessarily follow from the Hartree-Fock equations that the space part of orbitals corresponding to different spins are orthogonal to each other.

The second result which we shall prove regarding the solutions of the Hartree-Fock equations is Koopmans' theorem.[49] This theorem can be very simply stated in words, as follows: the one-electron energy ϵ_i corresponding to a wave function u_i forms a very good approximation to the ionization energy required to remove the electron with wave function u_i from the atom. Since these ionization energies are well known experimentally, those corresponding to the inner electronic shells being the x-ray term values, this forms a good and simple check between the calculations of the self-consistent field method and experiment. The agreement between the ϵ_i's and the term values was observed by Hartree in his earliest work on the self-consistent field. In fact, it was this agreement, as we have already noted, which was at the basis of the treatment of the self-consistent field even before quantum mechanics: we have quoted a number of workers who tried, partly empirically, to set up potentials such that the one-electron energies of particles moving in these fields would agree with the observed term values. The agreement between the two is better for the Hartree-Fock equations than for the Hartree equations, but still it is surprisingly good even for the Hartree equations. We shall now show how this agreement can be justified theoretically.

Clearly the way to find the energy required to remove a given electron from an atom is to compute the total energy of the atom with the given electron; then to compute the total energy of the atom lacking this electron; and to take the difference. This would properly imply solving a separate Hartree-Fock problem for the atom and the ion. All the one-electron orbitals would be slightly different, since the screening of each electron would vary depending on whether the electron were removed or not. There would be no way to compare the two problems, that of the atom and the ion, except by numerical calculations. Furthermore, the ionization energy is often a very small fraction of the total energy of the atom, so that we should be calculating two very large quantities, and taking the small difference, and this would be very inaccurate. This method is then not practicable, in most cases.

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[49] T. Koopmans, Physica 1, 104 (1933)

As a substitute, we may take advantage of the perturbation theory, which says that if we use a wave function which is wrong by a small quantity of the first order, the energy computed from it will be wrong by only a small quantity of the second order. We use this theorem in the following way. We use the correct Hartree-Fock wave function for the atom. For the ion, however, we make up a determinantal function out of the same one-electron orbitals found for the atom, but simply omitting the orbital related to the removed electron. We then compute the energy of the ion, using this determinantal function, which of course is slightly wrong. The energy is wrong by only small quantities of the second order, so that if we subtract this from the energy of the atom, the error in the resulting calculation of ionization energy will be small. But our calculations are made very much simpler, for now a great many terms in the energy are common to the calculation for both atom and ion, so that they automatically cancel. In fact, when we carry through the whole calculation, and subtract, the difference remaining is exactly the one-electron energy ϵ_i, all other terms cancelling. This is Koopmans' theorem, and we see that it shows the identity of the one-electron energy, and the ionization energy, up to terms of the second order of small quantities. We shall now show how this result comes about, from detailed calculation.

The calculation of the energy of the atom is carried through exactly as in the preceding section, in terms of Eqs. (1. 1) and (1. 5). For the ion, we merely omit the terms involving the wave function u_i, provided we are interested in the ionization energy of the ith electron. The difference, or the ionization energy, then consists of just the terms involving the function u_i. The energy of the atom minus the energy of the ion, which is the negative of the energy required to ionize the atom, is then

$$\int u_i^*(x_1)(-\nabla_1^2 - 2Z/r_1)\, u_i(x_1)\, dv_1$$

$$+ \sum(j) \int u_i^*(x_1)\, u_j^*(x_2)(2/r_{12})\, u_i(x_1)\, u_j(x_2)\, dv_1 dv_2$$

$$- \sum(j;\ \text{spin } j = \text{spin } i) \int u_i^*(x_1)\, u_j^*(x_2)(2/r_{12})\, u_j(x_1)\, u_i(x_2)\, dv_1 dv_2$$

We now substitute Eq. (1. 16), which is satisfied by $u_i(x_1)$, and we find at once that the result equals $\epsilon_i \int u_i^*(x_1)\, u_i(x_1)\, dv_1 = \epsilon_i$, on account of the normalization of the u_i's. Thus we prove Koopmans' theorem.

8. Extension of the Hartree-Fock Method

In the preceding sections, we have set up the Hartree-Fock equation, and have proved some properties of its solutions. We remember that this method is the appropriate one for finding the best one-electron orbitals for setting up a single determinantal wave function. It has several drawbacks, however. In the first place, it is rather hard to apply the method, in practice. It involves the calculation of a good many exchange integrals, and the orbital for each quantum number is a solution of a different Schrödinger one-electron problem. Secondly, in many cases we really wish to use a combination of a number of determinants, and in such a case the method is not directly applicable. No straightforward way appears for really getting around these difficulties; but in the present section we indicate some general lines of approach for extending the Hartree-Fock method to cases of the interaction of many determinants.

One approach is fairly direct. Suppose we have a problem of atomic multiplets, for which a number of determinants must be used. If this problem is not very complicated, we can solve for the energies of the various multiplet levels, in terms of certain exchange integrals (such as the F and G integrals encountered in the treatment of complex spectra given by the present writer). The energy of the ground state of the atom, then, can be expressed in terms of such integrals, which in turn depend on the one-electron orbitals. We then vary any one of the u_i's, in this expression for the energy of one of the states, and arrive at a differential equation, similar to the Hartree-Fock equation but containing additional terms, for this function u_i. These equations differ from the true Hartree-Fock equations only in that different expressions appear for the exchange charge density. The equations are not appreciably more difficult to solve by direct numerical methods than the Hartree-Fock equations, and the results should be very good. This method was used by Hartree and Hartree,(50) in a study of the excited states of the beryllium atom; they set up separate equations for the orbitals in the singlet and triplet state, and calculated separately the energy in these two states, getting much better agreement with experiment than by the use of the conventional Hartree-Fock method. The same method was also suggested simultaneously by Shortley.(51) It has not been widely used, and would be very difficult to apply if there were several multiplets of the same type, so that the secular equation of complex spectrum theory had to be solved numerically. For simple cases where an analytical solution is possible, however, it seems a desirable procedure. There is, however, a drawback: the orbitals for each state of the system are different, and in particular are not orthogonal to each other. The energy of each state must be computed for the whole system, rather than getting ionization energies directly by use of Koopmans' theorem. For a light atom like beryllium, to which Hartree applied the method, the total energy of the atom is not very big, and it is not difficult to compute this energy for each state, and subtract to get the multiplet separation. For a heavy atom, however, we should be subtracting one large quantity from another large quantity, and the inevitable errors would be serious.

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(50) D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) A154, 588 (1936).

(51) G. H. Shortley, Phys. Rev. 50, 1072 (1936).

A quite different approach to the problem would be, not to try to get the best orbitals to represent the energy of the state by means of simple complex spectrum theory, but rather to set up many determinants, and find linear combinations of them, relying on the large number of determinants for the accuracy of the answer, rather than on the correctness of a few determinants. In other words, we should make extensive corrections for configuration interaction; we should include determinants describing excited configurations of various types. There is much experimental evidence in spectroscopy for the importance of such interactions between configurations. Thus when there are large experimental deviations from the simple rules of multiplet separation suggested by the elementary theory of complex spectra, it often seems that these deviations may arise from the repulsion of states from different configurations which have proper symmetry and multiplicity properties so that they can have a nondiagonal matrix component of energy between them. An approach of this type has not been carried through in detail, but with our present improved ability to solve large secular equations, it should not be too difficult to carry out. If one wishes to do it, then the essential thing is to have a considerable number of determinantal functions representing different configurations, and orthogonal to each other. This demands orthogonal one-electron functions, corresponding not only to the ground state of the atom, but to a number of excited states, so that we can form determinants from a number of configurations formed from them. We may hope that if our orbitals and configurations are chosen properly, the most important determinants, for determination of the low-lying energy levels, will be those with only a few outer electrons excited. These would correspond to configurations with diagonal energies only slightly above the lowest state. And it is well known from elementary perturbation theory that states with diagonal energy close to each other have more perturbing effect on each other, other things being equal, than if they were further apart in energy.

We have already pointed out that the Hartree-Fock method, though it results in orthogonal orbitals, gives us only a small and definite number of those, corresponding to the orbitals occupied by electrons in the single determinantal state of the atom from which the Hartree-Fock equations are derived. We need more orbitals, corresponding to more highly excited states, for the determinantal method which we have sketched above, and the Hartree-Fock method does not tell us how to get them. We may use our intuition, however, to suggest an extension of the Hartree-Fock method which could give us as many orbitals as we desired. If the Hartree-Fock equations were only of the simple form of Schrödinger equations for one electron, then we could solve this Schrödinger equation for as many excited states as we desired, and these orbitals would all be orthogonal, by the fundamental orthogonality theorem of Schrödinger's equation. It seems very plausible, then, to try to replace the Hartree-Fock equations by an ordinary Schrödinger equation, expressing the motion of the electron in a single potential field representing somehow the effect of the nuclei and the other electrons.

8. EXTENSION OF THE HARTREE-FOCK METHOD

There is a straightforward way in which this can be done, though it does not seem to have been mentioned in the literature. Suppose we have an antisymmetric function $U(x_1 s_1 \dots x_n s_n)$, representing the motion of all n electrons. This is supposed to be a function which we arrive at in the process of solving a self-consistent problem. It may be a single determinant formed from one-electron orbitals, or a sum of a finite number of such determinants; or it may be any approximation to the real wave function of the system, in some particular stationary state, either the ground state or some excited state. Then we may ask the question, if an electron is found at position x, with spin s, and if all electrons move according to the wave function U, what is the average density of all other electrons, as a function of position, and hence what is the average potential exerted by these other electrons on the one in question, averaged over the position of the other electrons? We know that the probability that electron one be at position x_1 with spin s_1, and that simultaneously electron two be at position x_2 with spin s_2 is $\sum(s_3 \dots s_n) \int U^*(x_1 s_1 \dots x_n s_n)\, U(x_1 s_1 \dots x_n s_n)\, dx_3 \dots dx_n$. The probability that electron one be at position x_1 with spin s_1, irrespective of what the others are doing, is $\sum(s_2 \dots s_n) \int U^*(x_1 s_1 \dots x_n s_n)\, U(x_1 s_1 \dots x_n s_n)\, dx_2 \dots dx_n$. Thus the probability that electron two be at position x_2 with spin s_2, provided we know that electron one is at position x_1 with spin s_1, is the ratio of these two, or

$$\frac{\sum(s_3 \dots s_n) \int U^*(x_1 s_1 \dots x_n s_n)\, U(x_1 s_1 \dots x_n s_n)\, dx_3 \dots dx_n}{\sum(s_2 \dots s_n) \int U^*(x_1 s_1 \dots x_n s_n)\, U(x_1 s_1 \dots x_n s_n)\, dx_2 \dots dx_n} . \tag{1.18}$$

On account of the antisymmetry, we should have got the same sort of distribution for any one of the electrons 3 . . n as for the second electron. The total charge distribution of electrons 2 . . n, when the electron one is at x_1 with spin s_1, is then given by (n - 1) times the expression above. This is a function of the coordinate x_2 and spin s_2 of the second electron, so that it takes account of the possibility that there may be different charge densities for electrons of the two spins; and since it depends on s_1, these densities depend on which spin the electron one may have, so that we have the mechanism by which the spins of different electrons act on each other.

It is interesting to see what this charge distribution becomes for the special case where the wave function U is a single determinant of orbitals. In that case, taking advantage of the orthogonality of the orbitals, we can easily carry out the integrations in (1. 18), and we find that the charge density, (n - 1) times the expression (1. 18), is

$$\sum(j)\, u_j^*(x_2 s_2)\, u_j(x_2 s_2) - \frac{\sum(i) \sum(j)\, u_i^*(x_1 s_1)\, u_j(x_1 s_1)\, u_j^*(x_2 s_2)\, u_i(x_2 s_2)}{\sum(k)\, u_k^*(x_1 s_1)\, u_k(x_1 s_1)} \tag{1.19}$$

The first term of (1. 19) is just the total charge density of all electrons (since the index j goes from 1 to n). The second term is a correction or exchange charge, to be subtracted from this, so that the net charge will correspond to n - 1 rather than n electrons. This exchange charge density in (1. 19) is similar to that in Eq. (1. 17), which we derived from the Hartree-Fock equation. To get the exchange charge in (1.19) from that in (1.17), we multiply by a factor

$$\frac{u_i^*(x_1 s_1)\, u_i(x_1 s_1)}{\sum(k)\, u_k^*(x_1 s_1)\, u_k(x_1 s_1)} \tag{1.20}$$

and sum over i. The meaning of this is clear. In the Hartree-Fock method we find a different exchange charge density for an electron with coordinates x_1 and spin s_1, depending on which wave function u_k it is in. These exchange charge densities, as we showed in Section 7, have certain universal features: no matter which wave function the electron is in, the exchange charge density still integrates to one electronic charge, and still approaches the same limit when x_2, s_2 approach x_1, s_1. The exchange charge density (1.19), however, is the weighted mean of the densities (1.17) for the various states, using the weighting factor (1.20), which obviously measures the probability that, if electron 1 is found at position x_1 with spin s_1, it would be in the ith orbital.

It is the use of different exchange charge densities for the Schrödinger equations for the different orbitals which complicates the Hartree-Fock method. The present writer(52) has recently suggested that it could be simplified, without any serious errors being introduced, by using the weighted exchange charge density appearing in Eq. (1.19), in place of the separate exchange charge densities (1.17) appearing in the Hartree-Fock scheme. We now see, however, that the natural generalization of this scheme to the more general case where the wave function is a sum of determinants, rather than a single determinant, is to use the expression (1.18), multiplied by (n - 1), for the charge density of other electrons, to be used in computing the potential function for the self-consistent field.

Let us, following this discussion, write the Schrödinger equation for the one-electron orbital u_i, moving in the field of the nuclei, and of the charge densities of other electrons, as derived from the expression (1.18). To find the potential, at point x_1, of the charge density of other electrons, we multiply the expression (1.18) by $2/r_{12}$, and integrate over the coordinates and spin of electron 2; and multiply by (n - 1). We may equally well multiply by the sum of terms $2/r_{1j}$, summed over all j's except 1. Each of the $2/r_{1j}$ terms will give the same integral, on account of the symmetry properties of U. And the final answer, expressed in this way, is more symmetrical. If $V(x_1)$ is the potential energy of the electron 1 in the field of the nucleus or nuclei, then our Schrödinger equation is

$$\begin{aligned} &\left(-\nabla_1^{\,2} + V(x_1)\right) u_i(x_1 s_1) \\ &+ \left\{ \frac{\sum(s_2 \,.\,.\, s_n) \int U^*(x_1 s_1 \,.\,.\, x_n s_n)(2/r_{12} \,.\,.\, + 2/r_{1n})\, U(x_1 s_1 \,.\,.\, x_n s_n)\, dx_2 \,.\,.\, dx_n}{\sum(s_2 \,.\,.\, s_n) \int U^*(x_1 s_1 \,.\,.\, x_n s_n)\, U(x_1 s_1 \,.\,.\, x_n s_n)\, dx_2 \,.\,.\, dx_n} \right\} u_i(x_1 s_1) \\ &= \epsilon_i\, u_i(x_1 s_1) \end{aligned} \tag{1.21}$$

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[52] J. C. Slater, Phys. Rev. 81, 385 (1951).

We regard Eq. (1.21) as a very general formulation of the self-consistent field method. The potential energy function is a unique function, a function only of the position and spin of the electron 1. Thus all one-electron functions determined from it are automatically orthogonal to each other (though it is by no means true that the orbital parts of the functions associated with + spin are orthogonal to the orbital parts of those associated with - spin: the orthogonality in that case comes from the spin part of the functions). We can determine an infinite set of orthogonal orbitals by getting all solutions of (1.21). We then set up, by whatever method seems best to us, an approximate antisymmetric wave function for the whole system. We may well do this by setting up a finite number of determinantal functions, using the orbitals, following the methods outlined in the present chapter, and getting the best linear combinations of these determinants. We take that linear combination representing the state we are interested in (for instance, the ground state), and regard that as the function U, which enters in Eq. (1.21). We then make, as our requirement of self-consistency, the condition that the U computed in this way from the orbitals u_i should lead to a wave equation (1.21) which in turn has the same set of u_i's as its solutions.

We have determined the equation (1.21) by intuitive arguments, essentially as Hartree did with his first statement of the method of the self-consistent field, rather than by using arguments based on the variation principle, as with the Hartree-Fock equation. It is clear why this must be so. We have already shown that if we use enough determinantal functions, we can get a correct description of the final wave function, no matter what orbitals we use. We may well ask, then, what is the need of setting up our orbitals u_i by a self-consistent method like that of Eq. (1.21)? Why not just use any arbitrary orbitals? The answer apparently must be given intuitively, rather than by precise logic based on the variation principle, but it is this. If we use solutions of the self-consistent field, then we shall expect that those determinants formed from orbitals with the lowest one-electron energies ϵ_i, filling up the lowest states in the usual way, will have the lowest diagonal energies, and will come in in the most important way in the final linear combination of determinants. In other words, by use of these orbitals, we should be able to get a good approximation to the correct wave function with relatively few determinants, and we should be able to pick out these determinants by inspection, as those with the electrons in the lowest states, or with only a few excited electrons. On the contrary, with u_i's which depart widely from self-consistency, we should expect that far more determinants would be required to get a satisfactory approximation.

9. Free-Electron Gas Approximation to the Exchange Charge

Though we have been able, in Eq. (1.21), to set up a formulation of the self-consistent method general enough to give us one-electron orbitals u_i under all circumstances, still it can sometimes be very complicated to apply in actual calculations. A simplified version of the equation has been set up by the present author,[53] which preserves the main features of the correct method, but is a good deal easier to use and understand. We must remember that the electronic charge density represented by (1.18), multiplied by (n - 1), represents the charge of all electrons, diminished by the exchange charge density; we may, in fact, use this as a definition of the exchange charge density. This exchange charge density has a total amount of one electronic charge; this follows at once from the fact that the integral of the expression (1.18) over all values of x_2, and summation over s_2, is unity, so that the total charge density represented by (n - 1) times (1.18) is (n - 1) electronic charges. Furthermore, the expression (1.18) is zero when $x_1 = x_2$, and $s_1 = s_2$, on account of the antisymmetry of U. That is, the charge density of other electrons of the same spin as the first approaches zero as we approach the position of electron one. We may say, then, that the density of exchange charge of the same spin as the first electron approaches the total density of charge of that spin, as we approach the position of the first electron.

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[53] J. C. Slater, Phys. Rev. 81, 385 (1951).

We may, then, very crudely, replace the exchange charge density of the same spin as the electron one by a spherical charge distribution, whose density at its center equals that of all the electrons of spin s_1 at the point x_1, and of volume great enough to include one electronic charge. The volume, in other words, must be inversely proportional to the density of electrons, or the radius of the sphere must be inversely proportional to the 1/3 power of the density. The potential energy of an electron at the center of such a sphere will be inversely proportional to the radius of the sphere. Thus the potential energy will be directly proportional to the 1/3 power of the density. In other words, we approximately say that the potential energy to be used in the Schrödinger equation is the potential energy in the field of the nuclei, and of all the electrons, including the one whose wave function we are finding, diminished by a correction proportional to the 1/3 power of the density of electrons of the same spin as that considered. This replacement of all the exchange corrections by a term simply depending on the local charge density is obviously a great simplification, though of course it is not very accurate. We shall find later, when we discuss magnetism, that it gives useful qualitative insight into the magnetic problem, in that the potentials to be used for electrons of the two spins are not the same in a magnetic problem. If there is a preponderance of electrons of + spin, say, at a particular point, then the decrease of potential energy of a + electron, at this point, on account of the exchange correction, will be greater than for an electron of - spin, so that the potential energy of the electron of + spin will be lower. This distinction between the potential functions for electrons of the two spins, with consequent difference in the one-electron orbitals, should strictly be taken into account in self-consistent field work with atoms, but it has hardly ever been considered in actual calculations, up to the present.

When it comes to making this approximation method quantitative, we can take advantage of the free electron gas, for which the calculations can be made exactly. Bloch, (54) in the early days of quantum mechanics, discussed the magnetic properties of a free-electron gas.

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[54] F. Bloch, Z. Physik 57, 545 (1929).

He set up a single determinantal wave function for such a gas, using plane waves as the u_i's, filling up these waves far enough to accomodate all electrons. Then he essentially calculated the charge density of other electrons in the neighborhood of a given electron, essentially by use of (1.18). From this he found the exchange charge density exactly for this case, and integrated to find the corresponding correction term in the potential energy. We do not wish to take up this correction at this point, since it is concerned more with the problem of a solid than of an atom. When we work it out, however, we find that the Schrödinger equation for a function $u_i(x_1, +)$, where this symbolizes an equation for a function corresponding to + spin, can be written

$$\left(-\nabla_1^2 + V(x_1)\right) u_i(x_1, +) + \int \left(\rho_+(x_2) + \rho_-(x_2)\right) (2/r_{12})\, dx_2\, u_i(x_1, +) - 6\left(\frac{3}{4\pi}\rho_+\right)^{1/3} u_i(x_1, +) = \epsilon_i\, u_i(x_1, +)\,, \tag{1.22}$$

with a similar equation for $u_i(x_1, -)$. Here $\rho_+(x_1)$ and $\rho_-(x_1)$ represent the charge densities of charge of + and - respectively, at the point x_1, in atomic units, so that the term in $\rho_+ + \rho_-$ represents the potential of all electrons, at the point x_1. The term in $(\rho_+)^{1/3}$ is the exchange correction, of which we have been speaking. The exchange correction in Eq. (1.22) is, as we have stated, taken from the case of the free electron gas, and we are assuming that there is no great error if we replace the correct exchange interaction by this free electron value, computed for the same charge density which we actually have present. This of course is a crude assumption, but still, as we have stated, it is not qualitatively absurd. Calculations for the self-consistent fields of atoms, using Eq. (1.22), have been made by Pratt,(55) and he finds them in fairly good agreement with the more accurate Hartree-Fock method.

We have now come to the end of our sketch of the methods to be used in computing the energy levels of atoms; though no calculations have really been made following this complete scheme. It involves finding a set of orthogonal atomic orbitals u_i, as solutions of a Schrödinger equation, which should properly be Eq. (1.21), but which can be replaced by the cruder approximation (1.22). Having found these orbitals, we set up a number of determinantal wave functions, corresponding to the lower configurations of the atom. We solve the secular equation between these determinantal functions, so as to diagonalize the energy, taking full advantage of the properties of spin and orbital angular momentum. When we have done this, we obtain a wave function for each of the states derived from the secular equation. Since we are usually more interested in the ground state than of any other, we then take this wave function for the ground state, insert it, as U, into (1.21), and find a new Schordinger equation, repeating the process until we have self consistency. Or, if we are using (1.22), we compute the charge densities of electrons of + and - spin from the wave function, and seek self-consistency. It is clear that this process will be more accurate, the more determinants we take; and this

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[55] G. W. Pratt, Quarterly Progress Report of the Solid-State and Molecular Theory Group, M. I. T., July 15, 1952.

number, in the last analysis, will be fixed by the persistence of the computer, and the capabilities of his computing machines.

CHAPTER 2

THE HYDROGEN MOLECULE

The simplest quantum-mechanical problem with more than one atom is the hydrogen molecule-ion, H_2^+, the problem of a single electron moving in the field of two hydrogen nuclei. This problem of a single particle in the field of two centers attracting according to the inverse square law can be exactly solved, both in classical and quantum mechanics. One introduces ellipsoidal coordinates, with the two centers as foci, and finds that variables can be separated, so that in quantum mechanics the problem is reduced to that of solving ordinary differential equations. The solution, by Burrau,(1) has been of a good deal of qualitative value in understanding the nature of the problem of diatomic molecules. Unfortunately, however, the separability does not hold for any two-center problem except that involving inverse square forces, so that it cannot be applied to any diatomic molecule, in particular not to the hydrogen molecule. We must proceed by quite different methods, and Heitler and London,(2) whose work we have already quoted, made the first major effort to understand the structure of this simplest diatomic molecule.

This Heitler-London solution of the hydrogen molecule has been used so much, as a model for the solutions of more complicated molecules, that it will repay our very careful study. One feature of it, which we shall discover at the outset, makes its direct extension to more complicated problems impracticable: it deals with non-orthogonal orbitals, and we have seen in the preceding chapter how important it is to have orthogonal orbitals. A great deal of the literature of molecular theory is marred, as we shall point out in later chapters, by unwarranted neglect of the terms arising on account of this lack of orthogonality. Nevertheless we can recast the argument of Heitler and London in a form using orthogonal orbitals, and this we shall do, gaining in this way a starting point which can be extended to more complicated cases. When we do this, we find that an alternative point of view, the so-called method of molecular orbitals, is also included in our more general formulation. The present chapter takes up all these different approaches to the hydrogen molecule, and discusses their interrelationships, in such a form that they really can serve as models for our future work in more complex molecules and in solids. We shall find most of the problems encountered in the later chapters foreshadowed by features of this simplest of molecules.

1. The Heitler-London Method

As a first step, we remind the reader of the Heitler-London method itself. Heitler and London, we remember, wrote their famous paper in 1927, just after Heisenberg's 1926

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[1] Ø. Burrau, Kgl. Danske Vid. Selskab Skrifter, Mat-Fys. Med. 7, 14 (1927).

[2] W. Heitler and F. London, Z. Physik 44, 455 (1927); see also Y. Sugiura, Z. Physik 45, 484 (1927), for completion of some mathematical points left unfinished in Heitler and London's paper.

paper dealing with resonance phenomena in many-body problems, which we have discussed in the preceding chapter. Thus they were writing before the formulation of the determinantal method or the Pauli spin matrices, and they worked entirely with functions of the coordinates, as Heisenberg had done in his treatment of the helium atom. They argued in the following way. Let a represent a hydrogen 1s wave function about atom a, and b a hydrogen 1s wave function about atom b. Let the coordinates of the two electrons be denoted by x_1 and x_2. We know that, at least when the atoms are widely separated, the ground state will correspond to the situation where one electron is on one atom, the other on the other. Thus it could be represented by the wave function $a(x_1)b(x_2)$. It could equally well be represented, however, by the other function $b(x_1)a(x_2)$; these two functions will be degenerate with each other, at infinite internuclear distance. When now we try to solve a perturbation problem between these two functions, we find at once that the suitable linear combinations are the sum and difference, $a(x_1)b(x_2) \pm b(x_1)a(x_2)$, which are respectively symmetric and antisymmetric in the coordinates of the electrons. We can find the diagonal matrix components of energy for these two states, and find that the symmetric function has an energy minimum corresponding approximately to that known to exist in the ground state of the hydrogen molecule, while the antisymmetric function indicates repulsion between the atoms. By arguments similar to those used by Heisenberg in discussing the helium atom, in the papers cited earlier, Heitler and London identified the symmetric function with the singlet state, the antisymmetric one with the triplet state.

After the development of the determinantal method, the present writer[3] showed how this same argument could be stated in terms of orbitals involving spin as well as coordinates. Thus we may make a table, Table I, showing how the spins of the two electrons can be distributed among the two orbitals a and b. We can set up four determinants, associated with four assignments I -- IV of Table I. Thus the determinant corresponding to state I is

Table I

State	Spin of a	Spin of b	Total Spin
I	+	+	1
II	+	-	0
III	-	+	0
IV	-	-	-1

$$\begin{vmatrix} a(x_1)\alpha(s_1) & a(x_2)\alpha(s_2) \\ b(x_1)\alpha(s_1) & b(x_2)\alpha(s_2) \end{vmatrix},$$

where α represents the Pauli spin function, which is one when s_1 corresponds to a + spin, zero when s_1 corresponds to a - spin. That is, this determinant can be written $\{a(x_1)b(x_2) -$

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[3] J. C. Slater, Phys. Rev. 38, 1109 (1931).

$b(x_1)a(x_2)\}\,\alpha(s_1)\alpha(s_2)$. It is zero, in other words, unless both electrons have + spin, and it corresponds to an antisymmetric function of coordinates. Similarly the function IV is zero unless both electrons have - spin, and it has the same antisymmetric dependence on coordinates which we have just found.

The determinant corresponding to state II is

$$\begin{vmatrix} a(x_1)\alpha(s_1) & a(x_2)\alpha(s_2) \\ b(x_1)\beta(s_1) & b(x_2)\beta(s_2) \end{vmatrix},$$

and that corresponding to III is

$$\begin{vmatrix} a(x_1)\beta(s_1) & a(x_2)\beta(s_2) \\ b(x_1)\alpha(s_1) & b(x_2)\alpha(s_2) \end{vmatrix},$$

where β is the other spin function, zero when the spin is +, one when it is -. If we set up the matrix components of energy between states I -- IV, we readily find that there are no components between states I or IV and any other states, as we expect from the fact that M_S for these states (designated total spin in Table I) is different from the values for states II and III. We cannot uncritically use the formulas of Chapter 1 for components of energy, for the orbitals a and b are not orthogonal to each other; but the problem is simple enough so that we can handle the situation in spite of the lack of orthogonality, and check our statements. We find, however, that there are non-diagonal components of energy between states II and III, which are obviously degenerate with each other, so that as usual we find that the correct linear combinations are the sum and difference of II and III. As we see by expanding the determinants, this sum and difference equal

$$\{a(x_1)b(x_2) \mp b(x_1)a(x_2)\}\,\{\alpha(s_1)\beta(s_2) \pm \beta(s_1)\alpha(s_2)\},$$

where the upper signs are for the sum, the lower signs for the difference. We see, in other words, that the sum gives the same antisymmetric function of coordinates which we observed for states I and IV, and a symmetric function of spins, while the difference gives a symmetric function of coordinates, an antisymmetric function of spins.

It is then clear that the antisymmetric function of coordinates appears three times, for states of M_S = 1, 0, - 1, and hence this must correspond to the triplet state, while the symmetric function of coordinates appears just once, with M_S = 0, and hence must correspond to the singlet. Thus we verify the conclusions of Heitler and London regarding these functions. We can make these conclusions surer, if we wish, by computing the matrix components of the square of the magnitude of the spin, $S_x^2 + S_y^2 + S_z^2$, between these states, as we did in Chapter 1. Then we find unambiguously that our assignment of spins is correct; though here again, as with the matrix of energy, we must examine our steps with care, on account of the lack of orthogonality of the orbitals a and b.

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The net result, then, is that the orbital part of the wave functions associated with singlet and triplet respectively are $a(x_1)b(x_2) \pm b(x_1)a(x_2)$, where the + sign goes with the singlet, the - sign with the triplet. These functions are not normalized, but we shall normalize them in a moment. Then the diagonal matrix component of energy with respect to these functions must represent the energy of the two states. Let us compute this energy. First we normalize. We assume a and b to be separately normalized; but the overlap integral

$$\Delta = \int a(x_1)b(x_1)\, dx_1 ,$$

where we disregard the complex conjugate nature of the wave function a, since it is real, will not be zero. Thus we find that

$$\int \left\{a(x_1)b(x_2) \pm b(x_1)a(x_2)\right\}^2 dx_1 = 2(1 \pm \Delta^2) ,$$

so that the normalized wave functions are

$$\frac{1}{\sqrt{2(1 \pm \Delta^2)}} \left\{a(x_1)b(x_2) \pm b(x_1)a(x_2)\right\} .$$

We must now find the diagonal matrix component of the energy operator with respect to these two functions.

The energy operator is

$$-\nabla_1^2 - \nabla_2^2 - \frac{2}{r_{1a}} - \frac{2}{r_{2a}} - \frac{2}{r_{1b}} - \frac{2}{r_{2b}} + \frac{2}{r_{12}} + \frac{2}{r_{ab}} ,$$

where r_{1a} is the distance between the first electron and the nucleus a, etc., r_{12} is the distance between the electrons, and r_{ab}, which we shall denote by R, the distance between nuclei. We remember that the functions a and b are hydrogen 1s wave functions about the respective nuclei. Thus we have

$$\nabla_1^2 a(x_1) - \frac{2}{r_{1a}} a(x_1) = - a(x_1) .$$

where the coefficient - 1 multiplying $a(x_1)$ on the right side of the equation arises because the energy of the hydrogen ground state is - 1 atomic units. When we use this relation, we find that the energies of the two states are given by

$$E_{\pm} = - 2 + \frac{H_0 \pm H_1}{1 \pm \Delta^2} \qquad (2.1)$$

where

$$H_0 = \int a^2(x_1)b^2(x_2)\left(\frac{2}{r_{ab}} - \frac{2}{r_{1b}} - \frac{2}{r_{2a}} + \frac{2}{r_{12}}\right)dx_1dx_2 ,$$

$$H_1 = \int a(x_1)b(x_1)\, a(x_2)b(x_2)\left(\frac{2}{r_{ab}} - \frac{2}{r_{1b}} - \frac{2}{r_{2a}} + \frac{2}{r_{12}}\right) dx_1dx_2 .$$

We may rewrite these expressions as

$$H_0 = \frac{2}{R} + 2J + J', \quad H_1 = \frac{2\Delta^2}{R} + 2K\Delta + K' , \tag{2.2}$$

where

$$\begin{aligned}
J &= -\int a^2(x_1)(2/r_{1b})\,dx_1 \\
J' &= \int a^2(x_1)b^2(x_2)(2/r_{12})\,dx_1dx_2 \\
K &= -\int a(x_1)b(x_1)(2/r_{1b})\,dx_1 \\
K' &= \int a(x_1)b(x_1)\,a(x_2)b(x_2)(2/r_{12})\,dx_1dx_2 \,.
\end{aligned} \tag{2.3}$$

We have here chosen our notation, as far as the expressions J, J', K, K' are concerned, to agree with that of Pauling and Wilson, Introduction to Quantum Mechanics, McGraw-Hill, a convenient reference to use in looking up further details.

It was now shown in the papers of Heitler and London and of Sugiura, quoted above, how to compute the various integrals concerned. Their values are as follows:

$$\begin{aligned}
\Delta &= e^{-R}(1 + R + R^2/3) \\
J &= -2/R + e^{-2R}(2 + 2/R) \\
K &= -e^{-R}(2 + 2R) \\
J' &= 2/R - e^{-2R}(2/R + 11/4 + 3R/2 + R^2/3) \\
K' &= \frac{2}{5}\Big[-e^{-2R}(-25/8 + 23R/4 + 3R^2 + R^3/3) \\
&\quad + \frac{6}{R}\Big\{\Delta^2(\gamma + \ln R) + \Delta'^2\,\mathrm{Ei}(-4R) - 2\Delta\Delta'\,\mathrm{Ei}(-2R)\Big\}\Big] ,
\end{aligned} \tag{2.4}$$

where

$$\Delta' = e^{R}(1 - R + R^2/3) ,$$

where γ is Euler's constant 0.57722, and where Ei(x) is the integral logarithm (tabulated, for instance, in Jahnke-Emde's tables). In Table II we give values of these quantities, computed for a number of values of internuclear distance (in atomic units). The table includes also another quantity L, which we shall need later. From the quantities given in Table II we compute values of H_0, H_1, and $E_\pm$. These are given in Table III.

From Table III, we see that the singlet state, whose energy is E_+, has a minimum of energy at about 1.5 atomic units, corresponding to a stable ground state of the molecule, while E_-, the triplet state, is repulsive. The well known energy curves, plotted from these values, are shown in Fig. 1. In these tables and curves we have the predictions of the straightforward

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Heitler-London theory.

Table II

R	Δ	J	K	J'	K'	L
0.5	0.9603	- 1.7927	- 1.8196	1.2103	1.1353	1.1816
1.0	0.8584	- 1.4587	- 1.4715	1.1090	0.8733	1.0141
1.5	0.7252	- 1.1674	- 1.1157	0.9807	0.5937	0.8107
2.0	0.5865	- 0.9451	- 0.8120	0.8519	0.3683	0.6162
2.5	0.4583	- 0.7811	- 0.5746	0.7368	0.2132	0.4512
3.0	0.3485	- 0.6601	- 0.3983	0.6396	0.1170	0.3215
4.0	0.1893	- 0.4992	- 0.1832	0.4951	0.0312	0.1540

Table III

R	H_0	H_1	E_+	E_-
0.5	1.6249	1.3298	- 0.4629	1.7979
1.0	0.1916	- 0.1794	- 1.9930	- 0.5904
1.5	- 0.0208	- 0.3233	- 2.2255	- 1.3619
2.0	- 0.0383	- 0.2403	- 2.2073	- 1.6921
2.5	- 0.0254	- 0.1455	- 2.1412	- 1.8480
3.0	- 0.0139	- 0.0726	- 2.0834	- 1.9252
4.0	- 0.0033	- 0.0203	- 2.0228	- 1.9824

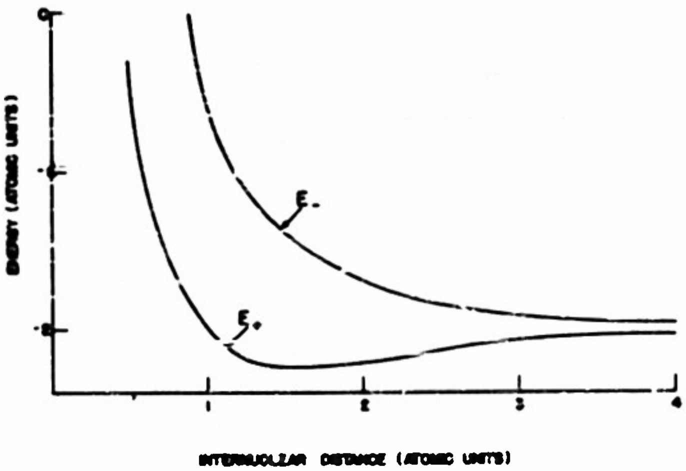

Fig. 1

Energy of hydrogen molecule as function of internuclear distance, Heitler-London theory. E_+, $^1\Sigma_g$ ground state. E_-, $^3\Sigma_u$ state.

2. Molecular Orbitals for the Hydrogen Problem

We have already mentioned the complications associated with the use of non-orthogonal orbitals, as in the Heitler-London method. These complications are not serious in a two-electron problem, but they rapidly become enormous as we go to problems of more and more electrons. Hence the Heitler-London method in its elementary form is not suited for generalization to more complicated molecules. We shall now show, however, that we can set up orthogonal orbitals, linear combinations of the two orbitals a and b used in the Heitler-London method, and that when we express the problem of the structure of the molecule in terms of these orbitals, it takes a form suitable for generalization.

As a guide in setting up these orthogonal orbitals, let us give a little attention to the method of the self-consistent field, as applied to molecules. In Section 8, Chapter 1, we set up a general self-consistent method which can be applied to molecules as well as atoms. We set up, in Eq. (1.21), a differential equation for the one-electron functions u_i. These represented the motion of an electron in a certain averaged field of the nuclei and the other electrons. We cannot hope to solve this differential equation exactly for a molecule; but at least we can hope to set up linear combinations of our atomic orbitals a and b which approximate as well as possible to solutions of this self-consistent field problem. Now in the hydrogen molecule problem, we should find the potential to be symmetric in the two nuclei; we shall later examine this problem of the meaning of Eq. (1.21) for this problem. And it is well known that in a two-center problem with symmetry in the nuclei, all solutions of Schrodinger's equation must be either symmetric or antisymmetric when the nuclei are interchanged. That is, the functions u_i must be either even or odd with respect to reflection in the plane midway between the two nuclei, with respect to which the nuclei are in the positions of mirror images. But there is only one way in which we can set up combinations of a and b having this property: the only even function is a + b, the only odd function, a - b. These functions are automatically orthogonal to each other, since their product is odd with respect to reflection in the midplane, and contributions to the overlap integral on one side of the midplane cancel contributions from the other side. Let us then set up these two orbitals. We may call them molecular orbitals, since this name has been applied to solutions of the self-consistent field problem for molecules, and our functions are approximations to those solutions.

We shall call the even function u_g, the odd function u_u (it is often convenient to use the symbols g and u, abbreviations of the German words gerade and ungerade, to denote even and odd functions). We readily find that the normalized functions are

$$u_g(x) = \frac{a(x) + b(x)}{\sqrt{2(1 + \Delta)}}, \quad u_u(x) = \frac{a(x) - b(x)}{\sqrt{2(1 - \Delta)}} .$$

We can now set up a table, similar to Table I, giving the possible arrangements of the two electrons in these two orbitals. This table, Table IV, is given below.

In Table IV, we have included six states, rather than the four given in Table I. Let us

Table IV

State	Spin of u_g	Spin of u_u	Total Spin
I	+ -		0
II		+ -	0
III	+	+	1
IV	+	-	0
V	-	+	0
VI	-	-	- 1

see why this is. If we find a one-electron energy for the orbitals u_g and u_u, we find that u_g lies lower than u_u; it is a general property of the symmetric and antisymmetric solutions of two center problems that the symmetric solution has a lower energy than the corresponding antisymmetric one. Thus in the language of the self-consistent field method, the lowest state of the molecule might well be assumed to come from the configuration where both electrons are in this lowest stationary state u_g. The electrons would have to have opposite spins, and to form a singlet state. It is this state which is represented by I, in Table IV. We should expect the next higher states to come when one electron is left in the u_g state, but one excited to the u_u state. In this case, since the electrons are not equivalent, we have a singlet and a triplet. These states come from the states III -- VI of Table IV: the states III, VI, and the sum of IV and V, represent the three components of the triplet, and the difference of IV and V is the singlet, just as in our discussion of the Heitler-London method, only now we are dealing with orthogonal one-electron orbitals, so that we can use exactly the method of Chapter 1 in solving the perturbation problem. Finally, the highest state would come when both electrons were excited to the u_u level, so that we should have the singlet given by state II of Table IV.

The two states which we omitted from Table I, corresponding to states I and II of Table IV, would be those in which both electrons were in atom a, or both in atom b. That is, the wave function would represent the situation where we had one positive ion, and one negative ion, so that we call such states ionic states. We know experimentally that it requires a considerable amount of energy to remove an electron from one hydrogen atom, and attach it to another atom. Thus these ionic states correspond to rather high energy levels of the hydrogen molecule, and we may expect that it will not make a great deal of difference in the wave function and energy of the ground state, whether we include them in our calculation or not. We shall later actually carry out the extension of the Heitler-London calculation to the case where these ionic states are present, and shall find in fact that they do not make much difference in the Heitler-London method, so that we understand how we could get a good value from the four states of Table I, while on the contrary we really need the six states of Table IV.

It is now very informing to take our definitions of u_g and u_u, and actually form the determinantal wave functions connected with the six states of Table IV. We may as well immediately form the sum and difference (properly normalized) of states IV and V, since we already know that these are the combinations which will diagonalize the quantity $S_x^2 + S_y^2 + S_z^2$. When we work out the functions, and write them in terms of a and b, we find the following:

$$\text{I:}\quad \frac{a(1)a(2) + b(1)b(2) + a(1)b(2) + b(1)a(2)}{2(1 + \Delta)}\;\frac{\alpha(1)\beta(2) - \beta(1)\alpha(2)}{\sqrt{2}}$$

$$\text{II:}\quad \frac{a(1)a(2) + b(1)b(2) - a(1)b(2) - b(1)a(2)}{2(1 - \Delta)}\;\frac{\alpha(1)\beta(2) - \beta(1)\alpha(2)}{\sqrt{2}}$$

$$\text{III:}\quad \frac{b(1)a(2) - a(1)b(2)}{\sqrt{2(1 - \Delta^2)}}\;\alpha(1)\alpha(2)$$

$$\text{IV + V:}\quad \frac{b(1)a(2) - a(1)b(2)}{\sqrt{2(1 - \Delta^2)}}\;\frac{\alpha(1)\beta(2) + \beta(1)\alpha(2)}{\sqrt{2}} \tag{2.5}$$

$$\text{VI:}\quad \frac{b(1)a(2) - a(1)b(2)}{\sqrt{2(1 - \Delta^2)}}\;\beta(1)\beta(2)$$

$$\text{IV - V:}\quad \frac{a(1)a(2) - b(1)b(2)}{\sqrt{2(1 - \Delta^2)}}\;\frac{\alpha(1)\beta(2) - \beta(1)\alpha(2)}{\sqrt{2}}.$$

When we examine these wave functions (2.5), we see that they have some resemblances to the Heitler-London wave functions, and also some differences. First we notice one thing: the triplet wave functions, the functions denoted by III, IV + V, and VI, are identical with the triplet functions given by the Heitler-London method, so that as far as they are concerned, we shall get the same answer by either method, and there is nothing more to do. We have, however, three singlet states, I, II, and IV - V, rather than the one singlet of the Heitler-London method. This is only natural, since we have started with six states rather than four, and clearly to get the corresponding three singlets out of the Heitler-London method, we should have to include the two ionic states there. Let us see how that would have worked out. The corresponding wave functions would have been simply

$$a(1)a(2)\;\frac{\alpha(1)\beta(2) - \beta(1)\alpha(2)}{\sqrt{2}},\qquad b(1)b(2)\;\frac{\alpha(1)\beta(2) - \beta(1)\alpha(2)}{\sqrt{2}}. \tag{2.6}$$

But now it can be shown that all real solutions of the hydrogen molecule problem must have wave functions which are either unchanged, or which change sign, when we reflect the whole wave function in the midplane between the two nuclei, or when we interchange the roles of atoms a and b. Thus if we set up the non-diagonal matrix component between the two states of Eq. (2.6), we find this component different from zero, and a perturbation problem set up just between these two states would result in solutions which would be proportional to the sum and difference of these two. These functions, even and odd in the nuclei respectively, are

$$\frac{a(1)a(2) + b(1)b(2)}{\sqrt{2(1 + \Delta^2)}} \quad \frac{\alpha(1)\beta(2) - \beta(1)\alpha(2)}{\sqrt{2}} ,$$
$$\frac{a(1)a(2) - b(1)b(2)}{\sqrt{2(1 - \Delta^2)}} \quad \frac{\alpha(1)\beta(2) - \beta(1)\alpha(2)}{\sqrt{2}} . \qquad (2.7)$$

We now notice first that the second of the states of Eq. (2.7) is identical with the state IV - V of Eq. (2.5). In either case, this is the only singlet state which is odd in the interchange of the nuclei. It is convenient to have a notation to describe the various properties of a state, and this notation is commonly set up in such a way that we would describe this state as ${}^1\Sigma_u$. The superscript 1 stands for a singlet, just as in an atomic configuration; the symbol Σ is analogous to S in an atomic case, and indicates that we have zero component of orbital angular momentum along the axis of the molecule; and the u indicates that the state is odd (ungerade) in the nuclei. Similarly the triplet state would be denoted ${}^3\Sigma_u$, since we observe that it also is odd in the nuclei. We are left, however, with two singlet states even in the nuclei, which we symbolize ${}^1\Sigma_g$, the g (gerade) standing for even. In the Heitler-London method, these are the ordinary singlet state, and the ionic singlet state given by the first of the two functions in Eq. (2.7). It is clear that the state I, Eq. (2.5), in the molecular orbital method, is the sum, and the state II the difference, of these two singlets given by the Heitler-London method (except that when we remember the normalization constants, I and II are linear combinations of the Heitler-London functions, but not as simple as the sum and difference).

We are now ready to consider the matrix components of the energy with respect to the six states of Eq. (2.5). There are of course no matrix components between two different states of different multiplicities. Furthermore, there are no matrix components between an even and an odd function in interchange of the nuclei; for in such a case, the contribution to the energy integral from one half of space is canceled by the contribution to the other. In other words, the only non-vanishing non-diagonal matrix component of energy will be between the two ${}^1\Sigma_g$ states I and II. Similarly in the Heitler-London method, the only non-vanishing component will be between the ${}^1\Sigma_g$ non-ionic and ionic states. Since there are two such states, we must solve a quadratic secular equation, which we may most conveniently solve between the states I and II of Eq. (2.5), since these are set up in terms of the orthogonal orbitals u_g and u_u. The final answer, however, will be the same as if we set up a secular equation between the ${}^1\Sigma_g$ non-ionic and ionic states of the Heitler-London method, for the two functions of one method are linear combinations of the two functions of the other. We shall shortly solve this secular equation. We notice that by introducing the functions of Eq. (2.5), in which each one is written so as to make $S_x^2 + S_y^2 + S_z^2$ diagonal, and in which each one is even or odd in the nuclei, we have secured the maximum simplification of the secular equation which is possible. The symmetry in the nuclei plays a role here somewhat similar to the orbital angular momentum in an atomic problem.

It is now a simple and straightforward task to set up the matrix components of energy between the various functions of Eq. (2.5). We can do this directly in the form written, where the functions are expressed in terms of a and b. Or we can set up the matrix components of the one- and two-electron operators with respect to the orthogonal orbitals u_g and u_u, and set up the matrix components of energy from these by the rules of Chapter 1. One method is about as convenient as the other, in this case, and by either method we set up the components in terms of the integrals defined in Eq. (2.3), and tabulated in Table II. We find that we need just two additional integrals. These are

$$L = \int a^2(x_1)a(x_2)b(x_2)(2/r_{12})\,dx_1dx_2 \ . \qquad (2.8)$$

which is tabulated in Table II, and

$$\int a^2(x_1)a^2(x_2)(2/r_{12})\,dx_1dx_2 = 5/4 \ . \qquad (2.9)$$

By methods similar to those of Heitler and London's paper, it can be easily shown that L is given by

$$L = e^{-R}\left(2R + \frac{1}{4} + \frac{5}{8R}\right) + e^{-3R}\left(-\frac{1}{4} - \frac{5}{8R}\right) . \qquad (2.10)$$

We may now write down the matrix components of energy. In the first place, for the states I and II in Eq. (2.5), we have the following diagonal and non-diagonal matrix components:

$$\begin{aligned}
H_{11} &= -2 + \frac{2}{R} + \frac{2(J+K)}{(1+\Delta)} + \frac{(K' + J'/2 + 2L + 5/8)}{(1+\Delta)^2} \\
&= -2 + \frac{2}{R} + \frac{(2J - 2K\Delta)(1-\Delta^2) + (K' + J'/2 + 5/8)(1+\Delta^2) - 4\Delta L}{(1-\Delta^2)^2} \\
&\quad + \frac{(-2J\Delta + 2K)(1-\Delta^2) + 2L(1+\Delta^2) - \Delta(5/4 + J' + 2K')}{(1-\Delta^2)^2} \\
H_{22} &= -2 + \frac{2}{R} + \frac{2(J-K)}{(1-\Delta)} + \frac{(K' + J'/2 - 2L + 5/8)}{(1-\Delta)^2} \qquad (2.11) \\
&= -2 + \frac{2}{R} + \frac{(2J - 2K\Delta)(1-\Delta^2) + (K' + J'/2 + 5/8)(1+\Delta^2) - 4\Delta L}{(1-\Delta^2)^2} \\
&\quad - \frac{(-2J\Delta + 2K)(1-\Delta^2) + 2L(1+\Delta^2) - \Delta(5/4 + J' + 2K')}{(1-\Delta^2)^2} \\
H_{12} &= \frac{(5/4 - J')}{2(1-\Delta^2)} \ .
\end{aligned}$$

The two ${}^1\Sigma_g$ energies will be the solutions of the secular equation formed from these components. Next, for the ${}^3\Sigma_u$ state, the energy has already been given as E_-, in Eq. (2.1)

Finally, for the ${}^1\Sigma_u$ state whose wave function is indicated as IV - V in Eq. (2.5), the energy is

$$-2 + \frac{2}{R} \cdot \frac{(2J - 2KA - K' + 5/4)}{(1 - A^2)} . \qquad (2.12)$$

In Table V we give values of H_{11}, H_{22}, H_{12}; the two energies $E({}^1\Sigma_g)_1$ and $E({}^1\Sigma_g)_2$ which are the two solutions of the quadratic secular equation; and the energy $E({}^1\Sigma_u)$ of the state (2.12).

Table V

R	H_{11}	H_{22}	H_{12}	$E({}^1\Sigma_g)_1$	$E({}^1\Sigma_u)_2$	$E({}^1\Sigma_u)$
0.5	- 0.4550	4.8109	0.2553	- 0.4674	4.8232	2.3089
1.0	- 1.9719	1.4077	0.2679	- 1.9930	1.4288	- 0.0547
1.5	- 2.1945	0.1173	0.2840	- 2.2289	0.1517	- 0.7937
2.0	- 2.1616	- 0.5536	0.3034	- 2.2170	- 0.4984	- 1.0854
2.5	- 2.0676	- 0.9256	0.3248	- 2.1535	- 0.8397	- 1.1984
3.0	- 1.9656	- 1.1505	0.3474	- 2.0935	- 1.0225	- 1.2384
4.0	- 1.7908	- 1.3730	0.3915	- 2.0256	- 1.1362	- 1.1994

In Fig. 2, we show the energies of all four terms, ${}^1\Sigma_{g1}$, ${}^1\Sigma_{g2}$, ${}^3\Sigma_u$, ${}^1\Sigma_u$, as a function of internuclear distance. We also show, for comparison, the quantities H_{11} and H_{22}, the diagonal energies of the two states I and II of Eq. (2.5), formed from single determinants of molecular orbitals, representing the configurations in which both electrons are in the orbital u_g, and u_u, respectively.

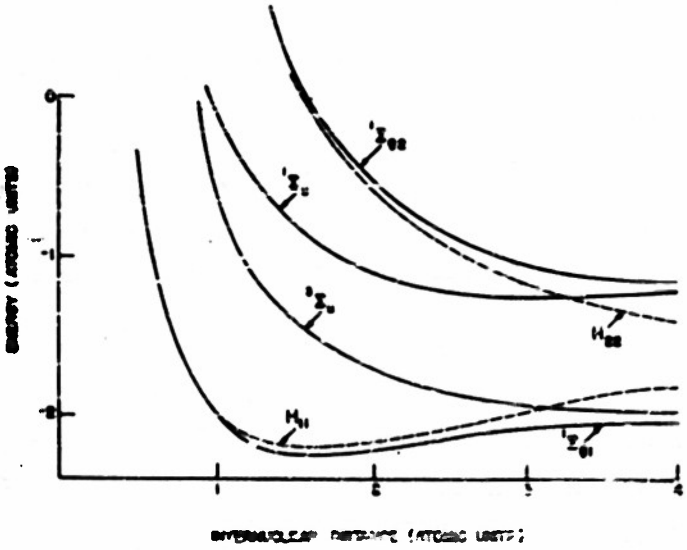

Fig. 2

Energy of hydrogen molecule as function of internuclear distance. Full curves, energies as derived from secular equation. Dotted curves, diagonal energies of ${}^1\Sigma_g$ states constructed from molecular orbital wave functions, without considering interaction.

We can now draw a number of conclusions from our calculations. In the first place, let us compare the energy $E({}^1\Sigma_g)_1$ of Table V, which represents the ground state as obtained by making linear combinations of our six determinants, and the energy of the state E_+ of Table III, which represent the Heitler-London approximation to the same state. It is clear from the comparison that the two agree very closely. The energy $E({}^1\Sigma_g)_1$ is slightly lower than E_+, as it must be by the variation principle; for $E({}^1\Sigma_g)_1$ is the energy of the best combination of the Heitler-London ground state and the ionic state of the same symmetry, and hence by the variation principle must have a lower energy than the energy of the Heitler-London ground state itself. But clearly the improvement in energy is very minor. Neither energy is a very good approximation to the actual ground state of hydrogen. The minimum at 1.5 atomic units is at about the correct internuclear distance to agree with experiment, but the binding energy of slightly under 0.23 atomic units is only about three quarters of the observed binding energy. Clearly the correction of this error is not to be sought by including ionic states in our calculation. We shall see later, by direct examination of the wave functions, that we do not actually make much alteration of the wave function of the Heitler-London ground state by including a contribution from the ionic state. The energy of the state $({}^1\Sigma_g)_2$ is so closely the same as the Heitler-London E_+ that we cannot tell the difference, on a figure of the scale used in Fig. 1 or 2.

Next, it is interesting to observe the limiting energy to which the two states ${}^1\Sigma_u$ and ${}^1\Sigma_{g2}$ tend at infinite internuclear distance. They both go, as we can easily see from Eqs. (2.11) and (2.12), to the limit $-2 + 5/4$. Here $5/4$ represents the integral of Eq. (2.9), the Coulomb repulsive interaction of two electrons both on the same atom. This is the approximation furnished by the present wave functions to the energy of a positive and a negative hydrogen ion at infinite distance. We represent the negative ion by having both electrons in the same orbital a on atom a. The energy is then the same as for two neutral atoms, except for the repulsive interaction of the two electrons on the same atom. It is now clear why these two states ${}^1\Sigma_u$ and ${}^1\Sigma_{g2}$ are missing in the usual Heitler-London formulation, since that formulation disregards the ionic states.

A further interesting observation concerns the diagonal energies H_{11} and H_{22} of the two states I and II, in Eq. (2.5). These energies go at infinite separation to the limit $-2 + 5/8$. The reason for this is clear from the wave functions, as written in Eq. (2.5). Here it is plain that each of these states, at infinite separation, goes into an equal mixture of the Heitler-London ground state, and the Heitler-London ionic state. Hence we should expect the energy to be the average energy of these two states, as it is. Putting it another way, in either the function u_g or u_u, the electron has equal chances of being found in either atom. At infinite separation, then, there are chances of 1/4 that both electrons be in atom a, 1/4 that both be in atom b, 1/4 that the first be in a, the second in b, and 1/4 that the second be in a, the first in b. The net result is a fifty percent chance of an ionic state. The interaction between these two states I and II, resulting from the secular equation, pushes the states apart, and it is clear that this repulsion of the states must persist to infinite internuclear distance. In order to result in the correct energy levels for the two ${}^1\Sigma_g$ states at infinite distance. We see, in fact, that the non-diagonal matrix component H_{12} responsible for pushing them apart, as given in Eq. (2.11), does actually approach the limiting value of 5/8 at infinite distance, so that there the two correct energies are $(-2 + 5/8) \pm 5/8$.

It is interesting to consider the actual values of the diagonal energy H_{11}, as given in Table V, and compare with the energy of the Heitler-London ground state E_r from Table III, or with the energy $E({}^1\Sigma_g)_1$ of the best ground state from Table V. We see that, in the neighborhood of the minimum, H_{11} is nearly as low as the correct energy level. In other words, the state L in which both electrons are in the molecular orbital u_g has a diagonal energy which is quite a good approximation to the best energy, near the minimum. This is the basis of the method of molecular orbitals, which we shall discuss in the next chapter. In that method, the wave function of a molecule is written as a single determinant formed from one-electron molecular orbitals. These molecular orbitals are generally approximated, as we are doing here, as linear combinations of atomic orbitals, so that the method is often known by that name (abbreviated LCAO). In the general case, as here, we shall find that the diagonal energy of such a one-determinant function goes to too high an energy at infinite separation; but sometimes it can form quite a good approximation to the actual molecule at its observed internuclear distance. We shall find later, too, that the method of energy bands, as applied to solids, is an extension of this method to solids, and that it has the same convenience, in that the wave function is written as a single determinant, but the same weakness, in that the limiting behavior at large internuclear distances is wrong.

Since the states I and II are orthogonal to each other, the sum rule applies; that is, the sum of the unperturbed energies equals the sum of the perturbed energies. In other words, the sum of H_{11} and H_{22} equals the sum of $E({}^1\Sigma_g)_1$ and $E({}^1\Sigma_g)_2$, or the average of H_{11} and H_{22} equals the average of $E({}^1\Sigma_g)_1$ and $E({}^1\Sigma_g)_2$. Still another way of expressing this is that the perturbation pushes the two states ${}^1\Sigma_{g1}$ and ${}^1\Sigma_{g2}$ apart by equal amounts from the diagonal energies H_{11} and H_{22}. This can be verified easily either from our formulas or from our tables of values. We also have another perturbation problem to which the sum rule applies: that between states IV and V of Table IV. This results in the states ${}^3\Sigma_u$ and ${}^1\Sigma_u$. Here the two unperturbed states are degenerate with each other, so that the diagonal energy of either one lies midway between the energies of ${}^3\Sigma_u$ and ${}^1\Sigma_u$ as given in Table V or Fig. 2. It is interesting that this diagonal energy is very nearly the average of H_{11} and H_{22} (though not exactly). The energy H_{11} represents the energy of the state with both electrons in the u_g orbital; states IV or V represent the energy of the state with one electron in u_g, one in u_u, and the state II, with energy H_{22}, is that with both electrons in u_u. The fact that the energy of state IV or V is nearly midway between H_{11} and H_{22} fits in with a one-electron interpretation of these states: raising one electron from state u_g to u_u raises the energy from H_{11} to the energy of IV or V, and raising the other electron raises it to H_{22}. Both of these involve approximately the same amount of excitation energy. This excitation energy is what would be computed by the molecular orbital method for molecules, or the energy band method for solids, as a measure of the energy required to change the one-electron energy as the electron goes from the symmetric to the antisymmetric orbital. This energy, for instance, goes to zero at infinite internuclear distance. We see by looking at Fig. 2, however, how violently modified the molecular orbital picture becomes, when we apply all the perturbations. The lowest and highest states are pushed apart from the energies H_{11} and H_{22} to $E({}^1\Sigma_g)_1$ and $E({}^1\Sigma_g)_2$, and the intermediate states are pushed apart to the energies of ${}^1\Sigma_u$ and ${}^3\Sigma_u$. We shall find later that similar things occur in the molecular orbital and energy-band theories, and there is where the most striking changes come about at large internuclear distances.

An important observation is connected with the sign of the exchange integral, which has pushed the two states ${}^1\Sigma_u$ and ${}^3\Sigma_u$ apart. From the simple theory of the spin degeneracy of two electrons, as sketched in Chapter 1, we see that when we have two states like IV and V, one corresponding to an electron of + spin in an orbital u_1, an electron of - spin in another orbital u_2, and the second corresponding to having the spins interchanged, we shall find the perturbed states split by an exchange integral

$$\int u_1^*(x_1)\, u_2^*(x_2)\, u_2(x_1)\, u_1(x_2)(2/r_{12})\, dx_1 dx_2 , \tag{2.13}$$

provided the orbitals are orthogonal. Such an integral is necessarily positive. For from its form it represents the Coulomb interaction energy of a charge distribution $u_1^*(x_1)\, u_2(x_1)$ on itself. Such an electrostatic energy can always be transformed, by methods familiar in electrostatics, to an integral of $\epsilon_0 E^2/2$, where ϵ_0 is the permittivity of free space, E the electric field, over all space. Since this integrand is everywhere positive, the integral must be positive. This sign is such that the triplet will always lie below the singlet, as we have in this case, with the ${}^3\Sigma_u$ lying below the ${}^1\Sigma_u$. Another case of the same result is found in atomic two-electron spectra, where the triplet always lies below the singlet. This is a special case of Hund's rule, given empirically in the days before the development of wave mechanics, according to which the multiplets of highest multiplicity tend to lie lowest in an atomic spectrum.

This rule is completely dependent on having orthogonal orbitals, as we see by comparison with the case of the Heitler-London method, where the orbitals are not orthogonal. The interaction between states II and III in Table I is of just the same sort which we have here, with that one exception; and yet the singlet lies lower in the perturbed problem, as we see from Fig. 1. The separation here depends on the exchange integral H_1, of Eq. (2.1), which is written out in detail in Eq. (2.2). When we examine the terms of H_1, we see that the terms in $2/r_{1b}$ and $2/r_{2a}$ are the ones which come in with negative sign, and which outweigh the positive terms, and result in a negative exchange integral H_1, as we see in Table II. These terms necessarily vanish if the orbitals a and b are orthogonal. Thus we see that any explanation of the binding of the molecule, resulting in a singlet ground state, in terms of a spin degeneracy, as in the method of Heitler and London, is impossible if we use orthogonal orbitals. We can see this more clearly in the next section, where we set up orthogonal orbitals A and B, rather similar to a and b in that A is concentrated on atom a, B on atom b, and yet orthogonalized to each other. When we use these orbitals, as we shall see, the triplet state lies below the singlet, and we are forced to take into account the interaction with the ionic states to get a correct picture of the ground state. Let us now proceed to this method of describing the molecule, for comparison with those already used.

3. Orthogonalized Atomic Orbitals

The molecular orbitals u_g and u_u are not the only orthogonal combinations of the orbitals a and b, which we can use for expressing our problem in terms of orthogonal orbitals. We can, of course, set up an infinite number of orthogonal combinations of a and b, but most of these would not appeal to us, for we naturally wish a certain amount of symmetry as regards the nuclei. Our functions u_g and u_u are particularly convenient in this way, in that the determinantal functions formed from them, as given in Table IV, automatically show the property of being symmetric or antisymmetric in the nuclei. The original functions a and b have a somewhat different symmetry property: one goes into the other when we reflect in the midplane between the atoms. Let us ask if we cannot set up two orthogonal orbitals A and B, linear combinations of a and b, which have this same property, so that the perturbation problem set up in terms of them will have as close a resemblance as possible to the Heitler-London problem. The answer is that we can. Let us demand that $A = c_1a + c_2b$, $B = c_1b + c_2a$, where c_1 and c_2 are to be chosen so as to make A and B normalized and orthogonal. We can impose this condition easily, and the determination of c_1 and c_2 becomes a simple problem in algebra. We find without trouble that

$$c_1 = \frac{1}{2\sqrt{1+\Delta}} + \frac{1}{2\sqrt{1-\Delta}}, \quad c_2 = \frac{1}{2\sqrt{1+\Delta}} - \frac{1}{2\sqrt{1-\Delta}}. \tag{2.14}$$

We see that c_1 is positive, c_2 negative. Furthermore, in the limit as internuclear distance becomes large, when Δ goes to zero, c_1 approaches unity, c_2 approaches zero, so that in this limit A and B approach a and b respectively. At smaller distances, however, c_1 decreases, c_2 increases numerically, so that A is made mostly of a contribution of a, but supplemented by a contribution of b with opposite sign, just large enough to make the two functions orthogonal. We shall indicate the relation of these orthogonal orbitals to others which have been proposed for molecular and solid-state problems in a later section.

Let us now set up our perturbation problem in terms of the orbitals A and B, and see how its results work out. By now, we realize that the final states will be exactly the same as those found by the method of molecular orbitals, or as found by the Heitler-London method supplemented by ionic states. But the steps encountered in getting the results will be quite different. What we are really doing is exploring a number of different methods of calculation, to see which one is most convenient for generalization to problems of more complicated molecules. We can set up a table, like Table I or Table IV, indicating the determinantal states which can be constructed out of the orbitals. By now, we realize that we must use all six possible determinants, so that while we have the four states like those of Table I, in which one electron is in orbital A, one in B, we must also have the two states in which both electrons are in one orbital. We can make linear combinations of these determinants, as before, to take advantage of our information about spin and symmetry. Thus the four states analogous to those of Table I will combine into a triplet, ${}^3\Sigma_u$, and a singlet, ${}^1\Sigma_g$. The two ionic states, in which both electrons are in A or both in B, will combine into two singlets, one of the nature of ${}^1\Sigma_u$, the other ${}^1\Sigma_g$. When we do this, we find, as we should expect by now, that the wave functions for the ${}^3\Sigma_u$ and the ${}^1\Sigma_u$ states are just as in the two previous methods, so that we have no new problem here. Only the two ${}^1\Sigma_g$'s are different.

Let us denote as ${}^1\Sigma_g{}'$ the state formed from the two determinants in which one electron is in A, one in B, and as ${}^1\Sigma_g{}''$ that in which both are in one orbital, analogous to the ionic state in the Heitler-London method. We then find that the two wave functions are the following.

$$\begin{aligned} {}^1\Sigma_g{}' &: \frac{a(1)b(2) + b(1)a(2) - \Delta\left\{a(1)a(2) + b(1)b(2)\right\}}{\sqrt{2(1-\Delta^2)}} \ \frac{\alpha(1)\beta(2) - \beta(1)\alpha(2)}{2} \\ {}^1\Sigma_g{}'' &: \frac{a(1)a(2) + b(1)b(2) - \Delta\left\{a(1)b(2) + b(1)a(2)\right\}}{\sqrt{2(1-\Delta^2)}} \ \frac{\alpha(1)\beta(2) - \beta(1)\alpha(2)}{2} . \end{aligned} \qquad (2.15)$$

The matrix components of energy between these states, which we shall denote H_{11}, H_{12}, H_{22}, are given by

$$\begin{aligned} H_{11} &= -2 + \frac{2}{R} + \frac{(2J - 2K\Delta)(1-\Delta^2) + (K' + J'/2 + 5/8)(1+\Delta^2) - 4\Delta L}{(1-\Delta^2)^2} - \frac{(5/4 - J')}{2(1-\Delta^2)} \\ H_{22} &= -2 + \frac{2}{R} + \frac{(2J - 2K\Delta)(1-\Delta^2) + (K' + J'/2 + 5/8)(1+\Delta^2) - 4\Delta L}{(1-\Delta^2)^2} + \frac{(5/4 - J')}{2(1-\Delta^2)} \qquad (2.16) \\ H_{12} &= \frac{(-2J\Delta + 2K)(1-\Delta^2) + 2L(1+\Delta^2) - \Delta(5/4 + J' + 2K')}{(1-\Delta^2)^2} . \end{aligned}$$

By comparison with Eq. (2.11), it is clear that the roots of the secular equation formed from these matrix components, derived from the orthogonalized atomic orbitals, will be the same as for the secular equation formed from the components of Eq. (2.11), formed from molecular orbitals. In fact, the interrelation between Eqs. (2.11) and (2.16) is so close that we can immediately read off the components of Eq. (2.16) from the entries of Table V. In Fig. 3, we show the energies of all four states ${}^1\Sigma_{g1}$, ${}^1\Sigma_{g2}$, ${}^3\Sigma_u$, and ${}^1\Sigma_u$, for comparison, as in Fig. 2, and the energies H_{11} and H_{22} computed from Eq. (2.16), the diagonal matrix com-

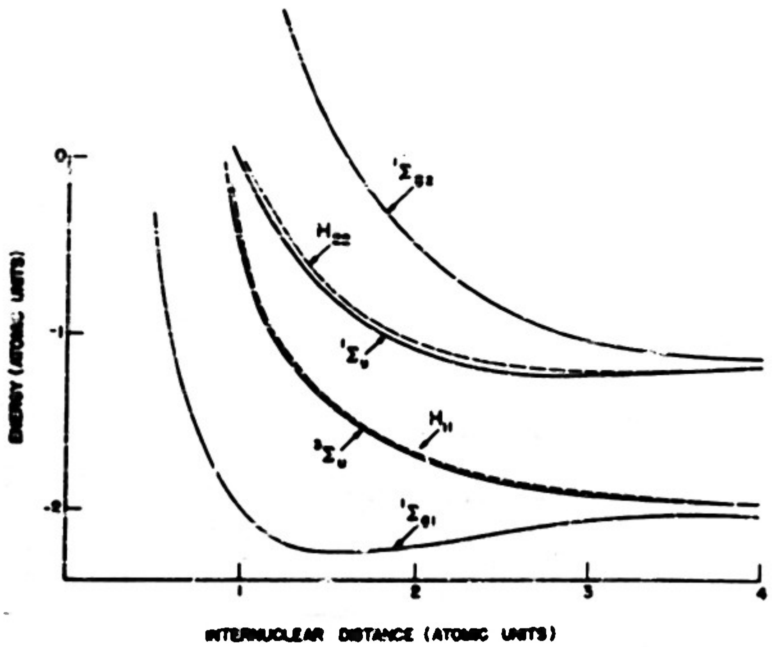

Fig. 3

Energy of hydrogen molecule as function of internuclear distance. Full curves, energies as derived from secular equation. Dotted curves. diagonal energies of ${}^1\Sigma_g$ states constructed from orthogonalized atomic orbital functions, without considering interaction.

ponents of energy for the two states ${}^1\Sigma_g'$ and ${}^1\Sigma_g''$ of Eq. (2.15).

We can now draw some rather striking conclusions from the results of Fig. 3. The state ${}^1\Sigma_g'$ is the one formed from orthogonalized atomic orbitals A and B, in just the same way that the ground state of the Heitler-London method is formed from the ordinary atomic orbitals a and b. In contrast to the Heitler-London ground state, shown in Fig. 1, which shows binding almost equal to that of the best function which we have set up, the state ${}^1\Sigma_g'$ of Fig. 3 shows no binding at all. The binding arises entirely in the secular problem between the two states ${}^1\Sigma_g'$ and ${}^1\Sigma_g''$. In other words, using orthogonalized atomic orbitals, it is imperative to carry out the mixing of the two states ${}^1\Sigma_g'$ and ${}^1\Sigma_g''$, of which the second is analogous to the ionic state in the Heitler-London method. This is a contrast to the Heitler-London case, where we have already seen that mixing in some of the ionic state makes a very small difference in the final energy of the ground state. We can see from Eq. (2.15) why there is this difference. The state ${}^1\Sigma_g'$, as we see from Eq. (2.15), is made up of a contribution from the function $a(1)b(2) + b(1)a(2)$, which is the Heitler-London ground state, but also a contribution, proportional to λ, of the function $a(1)a(2) + b(1)b(2)$, which is the Heitler-London ionic state. This latter function, coming in as λ increases, or as the atoms get closer together, completely neutralizes the attraction found in the Heitler-London ground state, and results in a repulsive state, as seen in Fig. 3.

It is clear from quite a different argument that this state must be repulsive. The two states $^1\Sigma_g{}'$ and $^3\Sigma_u$ are derived from a secular equation between the two states in which orbital A has an electron of + spin, B has one of - spin, or vice versa. This secular equation is like the Heitler-London secular equation, with the exception that the orbitals are orthogonal. Since they are orthogonal, the exchange integral between them must be positive, and the triplet state must lie below the singlet. We see from Fig. 3 that this is indeed the case. Furthermore, the rather small separation between singlet and triplet shows that this exchange integral is numerically small, in complete contrast to the Heitler-London case. Thus we see in still another way that the use of non-orthogonal orbitals is a necessary feature of the Heitler-London method. On the other hand, we must realize that it is only the simple Heitler-London method in which ionic states are not considered which is dependent on this use of non-orthogonal orbitals. The beauty of the Heitler-London method is that we do not have to solve a secular equation (aside from the trivial one involved in separating the singlet and triplet states) in order to get the ground state; the wave function can be written down by inspection. Once we include ionic states, however, we must solve a quadratic secular equation to find the ground state, and we have seen that the final result of solving this secular equation is the same, whether we use the Heitler-London functions including the ionic states, or the molecular orbital states, or those formed from orthogonal atomic orbitals. It is then this more general procedure, including ionic states, and using orthogonal orbitals of either the molecular or atomic variety, which gives us a method which can be generalized to the case of more complicated molecules.

4. Comparison of Various Wave Functions

In the preceding sections we have examined three different starting points, all leading to the same final result: the Heitler-London method supplemented by ionic states, the method of molecular orbitals, and the method of orthogonalized atomic orbitals. It is interesting to intercompare the wave functions resulting from these methods, so as to see, if possible, what their relations are. We have seen that all three starting points result in identical wave functions for the $^3\Sigma_u$ and $^1\Sigma_u$ states, so that we have no problem of comparison to carry out here. It is only with the two $^1\Sigma_g$ functions that we have differences. We can write these two functions, $^1\Sigma_{g1}$ and $^1\Sigma_{g2}$, as linear combinations of the Heitler-London ground state and ionic state; as linear combinations of the molecular orbital states I and II of Eq. (2.5); and as linear combinations of the orthogonalized orbital states of Eq. (2.15).

In examining the interrelations between these various functions, it is useful to use the concept of the scalar product of two vectors in a very literal sense. If we have two normalized functions u_1 and u_2, we know that we can regard them as unit vectors in a function space, and as far as these two vectors are concerned, this space is merely a plane, so that it is adapted to graphical discussion. Then the integral $\int u_1(x)\, u_2(x)\, dx$ is analogous to the scalar product of these two vectors, or to the cosine of the angle between them. We can then exhibit all the functions considered in our present discussion as unit vectors in a plane, and can find the angles between them. Let us find the angles between the various vectors, so that we can exhibit them graphically.

We know first, of course, that the two molecular orbital functions of Eq. (2.5) are orthogonal to each other; that means quite literally that the vectors representing them are at right angles to each other. Similarly the two functions of Eq. (2.15) are at right angles to each other. We may well first ask, what is the relation between these two sets of functions? If we take the scalar product of one of the functions of Eq. (2.5), and one of those of Eq. (2.15), we find that it is $1/\sqrt{2}$. This is the cosine of 45°; in other words, the two orthogonal vectors of one set form the bisectors of the angles between the two orthogonal vectors of the other set. We can in similar ways find the angles between the other sets of vectors. Thus we find that the cosine of the angle between the Heitler-London ground state and the ionic state is $2\Delta/(1 + \Delta^2)$. This is zero at infinite internuclear distance, where Δ is zero, so that in this limit the vectors are orthogonal; but at smaller distances it approaches unity, and the vectors become parallel to each other. This is the fundamental reason why we made such a small change in the energy of the Heitler-London ground state by adding some of the ionic state: we were really hardly changing the wave function at all, though we were writing it in quite a different way.

It is easy in similar ways to find the angles between all the various functions which we have considered. Thus we find easily that the cosine of the angle between the Heitler-London ground state function, and the molecular orbital ground state function, as given by function I, Eq. (2.5), is $(1 + \Delta)/\sqrt{2(1 + \Delta^2)}$. For the angle between this molecular orbital ground state function, and the final ground state function arrived at by solving the secular equation between states I and II, Eq. (2.5), we must remember that the final function may be written as a linear combination $T_1U_1 + T_2U_2$, where U_1, U_2 are the functions I and II of Eq. (2.5). From the linear equations determining the T's, we see that $T_2/T_1 = H_{12}/(H_{22} - E)$, where H_{12}, H_{22}, and E are given in Table V, the E for the ground state being denoted as $E(^1\Sigma_g)_1$ in that table. Since U_1 and U_2 are normalized and orthogonal, we know that $T_1^2 + T_2^2 = 1$, and that furthermore T_1 itself is the desired cosine of the angle between the function U_1 and the linear combination $T_1U_1 + T_2U_2$. We then find at once that

$$T_1 = \frac{1}{\sqrt{1 + H_{12}^2/(H_{22} - E)^2}}$$

Using these relations, we can then find the angles between the various vectors, or functions, in question. We show these in Table VI. We have referred all these angles to the direction of the final function representing the ground state, as zero, so that the final function representing the other $^1\Sigma_g$ state is in every case 90°. We show the angles of the following functions: the Heitler-London ground state; the Heitler-London ionic state; the molecular

Table VI

R	H-L Ground State	H-L Ionic State	M-O Ground State	O-A-O Ground State
0.5	1.6°	4.0°	2.8°	- 42.2°
1.0	0.1	8.8	4.5	- 40.5
1.5	- 2.2	15.9	6.9	- 38.1
2.0	- 4.3	24.9	10.3	- 34.7
2.5	- 5.6	35.2	14.8	- 30.2
3.0	- 5.6	46.0	20.2	- 24.8
4.0	- 3.0	65.6	31.3	- 13.7
∞	0.0	90.0	45.0	0.0

orbital ground state; and the orthogonalized atomic orbital ground state. From these, we can get the angle of the molecular orbital excited state by adding 90° to the angle of the molecular orbital ground state, and can get the angle of the orthogonalized atomic orbital excited state by adding 90° to the angle of the orthogonalized atomic orbital ground state. We observe that the angle of the molecular orbital ground state is 45° greater than that of the orthogonalized atomic orbital ground state, as it should be.

The first striking observation from Table VI is the closeness of the Heitler-London ground state to the correct wave function, as shown by the smallness of the angle between them. Through the whole range from infinite distances to small distances the angle is only a few degrees. We also see how small is the angle between the Heitler-London ground state and ionic state for small interatomic distances, though of course these two functions become orthogonal at infinite distance. It is this smallness of angle which, as we have already pointed out, makes it relatively unimportant whether we introduce some of the ionic state to correct the Heitler-London ground state. Then again, we notice the small angle between the molecular-orbital ground state and the correct function, at small internuclear distances. It is this small angle which results in the approximate correctness of the molecular orbital function near the actual internuclear distance. On the other hand, we see that this angle approaches 45° at infinite internuclear distance, explaining the failure of the molecular orbital method at large distances. Finally we note that, though the orthogonalized atomic orbital ground state is correct in the limit of infinite internuclear distance, it becomes extremely poor near the actual internuclear distance.

With this comparison of wave functions, we have finished our study of the various approximations to the hydrogen problem arising from simple use of determinantal wave functions based on the 1s atomic orbitals on the two atoms. A comparison of the type discussed in this chapter seems to have been first given by the present writer,(4) in a paper in which the results were presented graphically; the calculations on which the graphical discussion was based were

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[4] J. C. Slater, Phys. Rev. 35, 509 (1930); 41, 255 (1932).

identical with those of the present chapter. A later discussion by Weinbaum(5) carried through similar calculations, but extended them by varying the 1s atomic functions out of which the molecular functions were constructed; these 1s functions were given variable parameters which were varied as a function of internuclear distance, to get a minimum energy for the ground state, resulting in appreciable improvement in the wave function and energy at the observed internuclear distance.

Discussion of the comparison between the various wave functions, of the sort given in the present section, was given by the present writer(6) in a paper whose main purpose was to examine the usefulness of the orthogonalized atomic orbitals for problems in molecular structure. Functions of this type had been introduced by Wannier(7) for use in crystal problems, and had been extended to molecular problems by Löwdin,(8) who has also made much use of them in the study of solids. We shall have much further use for functions both of this type, and of the molecular orbital type, in our further study.

It should not be thought that a comparatively simple treatment of the hydrogen molecule, such as we have discussed in this chapter, represents all that has been done on this important problem. We have presented these simple calculations only on account of their direct application to further problems of more complicated molecules. There have been, however, a great many papers written on the theory of the hydrogen molecule, though we shall not quote many of them here. We give later in this report a very full bibliography of papers on all branches of the theory of the electronic energy levels of molecules, and many papers in that bibliography deal with hydrogen. Many of them were undertaken with a view of throwing light on more complicated problems of molecular structure, and we shall comment on them at suitable points in later chapters. Two of them, however, are so straightforward that they deserve some comment at this point.

In the first place, one very obvious improvement in the theory as we have presented it would be to vary the size of the atomic orbitals out of which we have constructed our wave functions, in a way depending on internuclear distance. At infinite separation, it is reasonable that we should use hydrogen orbitals, but as the nuclei approach each other, the problem approaches that of a helium atom, which it reaches when the nuclei come into contact. This helium atom has a self-consistent solution in which the wave functions are hydrogen-like, but corresponding to an effective nuclear charge nearer two units than one; as a matter of fact, hydrogen-like wave functions corresponding to a nuclear charge of 1.6875 units prove to represent the best approximation. We should expect, then, that we could improve matters considerably if we carried out an analysis just like that of the present chapter, but used for each

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[5] S. Weinbaum, J. Chem. Phys. 1, 593 (1933).

[6] J. C. Slater, J. Chem. Phys. 19, 220 (1951).

[7] G. Wannier, Phys. Rev. 52, 191 (1937).

[8] P.-O. Löwdin, J. Chem. Phys. 18, 365 (1950).

internuclear distance an atomic orbital which would not be proportional to e^{-r}, the hydrogen-like function (where r is in atomic units), but e^{-Zr}, where Z is an effective nuclear charge, which may be expected to vary from 1 at infinite separation, to 1.6875 as the separation goes to zero. It is easy to carry out this calculation: all the integrals are essentially as in the present chapter, but with factors multiplying them which are as simple as Z or Z^2. In the final answer for energy, then, we vary Z to make the energy a minimum, for each internuclear distance. Such a calculation was first made by Wang,(9) and was extended by Weinbaum, in the paper already referred to, and has been used and extended by other writers. It makes a very significant improvement in the energy, reducing the discrepancy between the observed and calculated energies of the ground state, at the equilibrium distance, to about two thirds of the value found by the Heitler-London method.

A very much greater improvement was made in 1933 by James and Coolidge,(10) whose work has become a classic of careful numerical solution of Schrödinger's equation. James and Coolidge gave up the attempt to build up a wave function by starting with atomic wave functions, but instead considered directly the form of the differential equation, and the best methods of approximating its solution. Let us consider the problem in the following way (though this is not precisely the method James and Coolidge used). The first electron may be described by three variables, of which two are coordinates in a plane passing through the electron and the two nuclei, and the third is the angle of rotation of this plane with respect to a fixed plane through the nuclei. Similarly the second electron may be described by two variables in the plane passing through it and the nuclei, and by the angle of this second plane. The whole wave function of the ground state will not depend on all of these six variables, however: for on account of the fact that its component of orbital angular momentum around the axis of the molecule is zero, it can be shown that only the difference of the angles, or the angle between the two planes, can enter the solution, and not either angle separately. Thus there are really only five variables determining the wave function. James and Coolidge now set up a series of terms depending on these five variables, falling off exponentially as both electrons went far from the nuclei, so as to insure proper behavior of the wave function at infinity, and chosen so that a combination of these functions would be almost sure to be flexible enough to represent the true ground state accurately. As parameters, they used the coefficients of these various functions, and they computed the energy as a function of the parameters, and varied the parameters so as to get a minimum value of energy.

They carried out their procedure by starting with a rather small number of functions, minimizing the energy, and then adding a term at a time, to see how much improvement they got. They continued the process up to something of the order of fourteen terms, at which point the addition of further terms was making a negligible improvement. The net result of

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[9] S. C. Wang, Phys. Rev. 31, 579 (1928).

[10] H. M. James and A. S. Coolidge, J. Chem. Phys. 1, 825 (1933), and later papers.

this was that their final energy differed from the observed energy of the molecule by a quantity of the order of magnitude of the experimental uncertainty in this energy. In other words, they had done two things: they had produced a wave function which was a practically perfect solution of Schrödinger's equation, in the form of a sum of a number of analytic terms; and they had verified that the solution of Schrödinger's equation agrees with experiment with great accuracy in this case. This latter point should not be overlooked, in evaluating the importance of their result. Aside from the hydrogen atom and a few soluble problems, the successes of Schrödinger's equation have been mostly qualitative, on account of the great difficulty of getting accurate numerical solutions. Very few many-body problems have been carried through with very great accuracy. One of these is the ground state of the helium atom; Hylleraas,(11) some years before James and Coolidge, had used a very similar method for this problem, and had likewise found a result agreeing with experiment to practically spectroscopic accuracy. The hydrogen molecule is practically the only other case. The very good agreement in both these cases has convinced everyone that the Schrödinger equation really does agree with experiment for the many-body as well as the one-body problem, and this encourages us to take the further steps to be described in these notes, approximating more and more closely to problems of more complicated molecules and of solids, confident that the results will approach experimental values more and more closely, the further we carry our approximations. This confidence is at the very foundation of our theory of molecules and solids, and it is based more than anything else on the careful calculations of Hylleraas and of James and Coolidge which we have just quoted, together with the other aspect of the problem, the widespread qualitative agreement between experiment and the theories of multiplet structure and such things provided by our approximate methods.

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[11] E. Hylleraas, Z. Physik 48, 469 (1928).

CHAPTER 3

THE METHOD OF MOLECULAR ORBITALS

Following the work on the hydrogen molecule which we have described in the preceding chapter, there has been a very large amount of theoretical work on the structure of molecules of all sorts. We shall present later a bibliography of the papers on this subject; it comes to many hundreds of papers. It is obvious that we cannot quote all this work, or give references to it as we proceed, and in our discussion we shall generally merely mention the principal workers in the field and the nature of their contributions, leaving it to the reader to locate their papers in the bibliography.

The first thing to notice about this great literature is that it is rather sharply divided into two main schools of thought. One of these developed directly from the work of Heitler and London, trying to set up wave functions for complicated molecules by direct analogy with the Heitler-London function for hydrogen. We shall discuss these methods in the next chapter. They suffer from two great drawbacks. In the first place, they deal with non-orthogonal atomic orbitals, as the Heitler-London method does; in the second place, they must use a linear combination of determinants to get a representation of the ground state. The second school of thought developed from the fact that the molecular orbital type of wave function, which we mentioned in the preceding chapter, itself forms a fairly good approximation to the ground state of molecules. This method is more convenient than the Heitler-London method in that it deals with a function which is made up as a single determinant, and the molecular orbitals which it uses are automatically orthogonal. It is thus simple to use. It has the compensating drawback that, as in hydrogen, it does not reduce to the correct limiting values at infinite internuclear separation. For this reason, work with the molecular orbital method has generally been carried out only at the equilibrium internuclear distance or close to it, and there it has shown itself capable of giving a great many valuable results. On account of its simplicity, we shall describe this molecular orbital method first, devoting the present chapter to it. Then in the next chapter we shall consider methods which involve taking linear combinations of determinants. This includes the extension of the Heitler-London method to complicated molecules, but it also includes the general method of configuration interaction, similar to what we have described in Chapter 1 for atoms. That method in its general form is more inclusive than the Heitler-London procedure, and represents the best method which we have for approximating to the solution of Schrödinger's equation for molecules and solids.

1. The General Nature of the Molecular Orbital Method

The molecular orbital method has grown up somewhat gradually, and it has become clarified as it has developed. Before we trace this historical development, we wish to know clearly what the method is. In the present section, therefore, we shall state what we shall mean by the method. Then we shall go on in later sections to describe its history, and to state the various approximations which have been used to carry it through in practice.

Briefly, the method is a straightforward application of the method of the self-consistent field. We assume that we solve a one-electron problem for the motion of an electron in the field of the nuclei, and the averaged charge distribution of all other electrons. The resulting wave functions are called molecular orbitals. Each will have its one-electron energy, as in the atomic case, and as in that case we can show by Koopmans' theorem that these one-electron energies approximate the energy required to remove the corresponding electron from the molecule. We then build up the ground state of the molecule by filling up these wave functions, starting with those of the lowest one-electron energies, with one electron each (for each spin), until we have accomodated all electrons. We note that Koopmans' theorem, by a slight extension, indicates that this should represent the state of lowest energy. For we can argue, as we do in the study of x-ray term values, that the energy required to move an electron from one energy level to another is approximately the difference of the one-electron energies of the two levels, so that certainly the energy of the whole system will decrease if we go from a state in which one inner level is unoccupied, to another in which an electron has fallen from an upper level into this previously unoccupied inner level. In other words, we can justify the elementary picture that all electrons want to fall into the lowest possible energy levels, to get the ground state.

In an atom, in a similar way, we set up the configuration of the ground state by filling all one-electron levels in order of increasing energy. From each resulting assignment of electrons to wave functions, we set up a single determinantal function. With atoms, we have seen that on account of orbital and spin degeneracy, we very often have a number of such determinants whose diagonal energies are about the same, so that we must treat the degeneracy problem between these determinants by solving a secular equation, resulting in a linear combination of the resulting determinants. With molecules, on the contrary, in a great majority of the cases we find that there are just enough electrons to fill certain one-electron functions, and that there is a considerable difference in energy between this configuration, and any other configuration formed by putting certain electrons in other orbitals. Thus in the case of H_2, we have found two orbitals, which we called u_g and u_u, which are the two lowest orbitals in the problem from the standpoint of energy. With our two electrons, we can put one of each spin in the u_g orbital, to represent the ground state. If one is removed from this orbital, the next higher state comes if it is in the u_u orbital, the remaining one being in u_g, and our discussion of Chapter 2 has shown that this corresponds to a considerably higher energy. Thus a single determinant corresponding to the two electrons being in the u_g orbital, one with each spin, represents by itself a good approximation to the ground state, and it is this which we have described as the molecular orbital function, in Chapter 2.

Similarly in a great majority of molecules we can represent the ground state by a single determinant; and the molecular orbital method is just that in which this single determinant is used as an approximate wave function for the molecule. Having formed the determinantal wave function, we can then proceed to find a potential from it, and to use this potential as the starting point of a further stage of the self-consistent method. Since we are dealing with a single determinant, we have a case to which the Hartree-Fock method is directly applicable. On the other hand, if we are interested eventually in interactions with higher configurations, so that we wish to find a set of orthogonal orbitals, we will do better to use the extension of the Hartree-Fock method described in Eq. (1.21), since this will give a single potential function for all the orbitals. In most of our descriptive discussion we shall assumed that this method of Eq. (1.21) is used, though in some of the applications a method closer to the Hartree-Fock has been applied.

It is not an accident that most molecular problems can be approximated by a single determinant. We recall the atomic cases where a similar approximation is good: we have such a case when the ground state is a ^1S state, and this results when the electrons form a closed shell, as in the inert gas atoms. Ever since the original suggestions of G. N. Lewis on the nature of valence, the chemists have believed that there was a strong connection between the existence of stable molecules, and the formation of a closed shell of some sort by their outer electrons. This is only a qualitative idea, which can be made more precise as we go further into the theory; but it makes it seem very likely that the reason why many molecules have a ground state which can be approximated by a single determinant is the simple fact that it is these molecules which are stable, and which are ordinarily formed in nature. There are of course some exceptions to this rule, but they are relatively unimportant. And of course in the excited states of molecules, we no longer have this simplification, and must use combinations of determinantal functions. The ground states, however, are particularly appropriate for the use of the molecular orbital method, on account of this fact that generally they can be well described by a single determinantal function.

We have talked of this self-consistent calculation as if it were a simple and straightforward thing, and in principle it is. In practice, however, it is so hard that hardly any molecule has ever been carried through by it; the only really serious attempt to use it in detail has been that of Coulson(1) on H_2, where by methods similar to those of James and Coolidge, he obtained molecular orbitals much closer to self-consistency than the simple combinations a ± b which we have mentioned in Chapter 2, and got a corresponding lowering of the energy of the molecular orbital state; though it still was about as far above the correct energy of the ground state as the molecular orbital energy which we have discussed in Chapter 2 was above the lowest energy calculated by the methods of Chapter 2. The reason for this difficulty is obvious: we have to solve a one-electron problem of the motion of an electron in the field of many centers, and this problem, unlike the corresponding central-field problem for an atom, does not permit separation of variables, and is very hard to solve accurately by any approximation method. Accordingly we must look for the best methods we can find for

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[1] C. A. Coulson, Proc. Cambridge Phil. Soc. 34, 204 (1938).

approximating to such a solution, and we shall discuss this further in the present chapter. Even if we have found an approximate wave function, we still have further difficulties ahead, for we must find the diagonal matrix component of the whole energy, in order to get the total energy of the molecule, and this involves integrals which may be very hard to evaluate. As a matter of fact, most of the work which has been done so far has contented itself with a calculation of the one-electron energies, and has not carried through the whole calculation of the energy of the molecule.

2. The Historical Development of the Molecular Orbital Method

With the sketch which has been given in the preceding section, we understand what the molecular orbital method is well enough so that we can now go back intelligently and consider its development. The names of three physicists are connected with its origin, more perhaps than of any others: Hund, Mulliken, and Lennard-Jones. Mulliken and Hund had been working at the analysis of the electronic spectra of diatomic molecules, even before the beginning of wave mechanics in 1926. We realize, of course, that each electronic energy level of a diatomic molecule corresponds to a curve of energy as a function of internuclear distance. This curve represents the energy of the electronic system, including electronic kinetic energy, electronic potential energy in the fields of the nuclei and of each other's repulsions, and the nuclear repulsive energy, as a function of distance, when the nuclei are assumed to be held fixed. Hund and Mulliken were engaged in applying the ideas of the vector model and complex spectrum theory to the observed molecules, at the time when wave mechanics was invented. It was very natural, since the energy levels of the separated atoms could be explained by the self-consistent field method, plus the interactions between angular momentum vectors treated in complex spectrum theory, to suppose that a similar method could be used for the combined molecule as well. And in this way they began to think of a molecule as built up from one-electron wave functions which were solutions of the two-center problem, the lowest one-electron energy levels being filled far enough to accomodate all the electrons, and the upper ones being empty, though occupied in excited states.

The problem of the solutions of the two-center problem thus became of great importance. The first case of this sort that was accurately solved was that of the hydrogen molecule-ion, whose solution by Burrau(2) has already been mentioned. This exact solution, however, was less useful than the approximate solution made up as a linear combination of atomic orbitals, such as we have discussed in the preceding chapter; this way of approximating to the two-center problem was discussed, among others, by Pauling(3) and by Morse and Stueckelberg.(4) Then in 1929 Lennard-Jones, in an important paper,(5) considered the

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[2] Ø. Burrau, Kgl. Danske Vid. Sels., Mat.-fys. Med. 7, 14 (1927).

[3] L. Pauling, Chem. Revs. 5, 173 (1928).

[4] P. M. Morse and E. C. Stueckelberg, Phys. Rev. 33, 932 (1929).

[5] J. E. Lennard-Jones, Trans. Faraday Soc. 25, 668 (1929).

probable nature of the energy levels as a function of internuclear distance. in the problem of two attracting centers which represented successively the self-consistent fields for the molecules Li_2, Be_2, B_2, C_2, N_2, O_2, and so on. It was of course too hard to get exact or even approximate solutions for these two-center problems, but by piecing together various sorts of information, Lennard-Jones was able to deduce the general form of the energy levels, and to find which were the lowest, and consequently which ones were occupied in the ground state of the molecule. In this way he arrived at information about the ground states, and was even able to explain why the molecule O_2 is paramagnetic, having a triplet state as its ground state.

These general principles were rapidly extended, by Hund, Mulliken, Herzberg, and others in the next few years, to give a good description of the structure of the diatomic molecules, both homopolar (consisting of two like atoms) and heteropolar (having two different atoms). It was a natural step to start on the polyatomic molecules, and Mulliken started in 1932 writing papers about polyatomic molecules; for these, and the large literature of the subject, the reader is referred to the bibliography. In one particularly important paper,(6) he discussed the symmetry of the electronic wave function, arising from the symmetry of the molecule. Thus in a homopolar diatomic molecule, we have seen that the wave function must be symmetric or antisymmetric on reflection in the plane midway between the atoms. This is merely the simplest example of a very general set of symmetry principles, which we shall examine in a later section. The general formulation of these symmetry principles is best given by the group theory; but in many important cases the results are simple enough so that they can be understood by inspection. In any case, in a polyatomic molecule, we no longer have the conservation of angular momentum, and the consequent orbital angular momentum and its related quantum numbers, to help us in our problem of classifying the orbitals and helping in factoring the secular equation. We do, however, have these symmetry properties, and they fulfill many of the same functions. Thus a study of such symmetrical molecules as methane, ammonia, and many others, really demanded the study of the symmetry, and the nature of the molecular orbitals and structure of these molecules advanced rapidly.

Shortly before the papers of which we have just spoken, Hückel,(7) in a very important set of papers, laid the foundation for the theory of the benzene molecule. Earlier he and others(8) had attacked the problem of the carbon double bond, and the application of this to the benzene problem was obviously desirable. Let us recall for the non-chemical reader the particular problem of the benzene molecule. We recall that it is a regular hexagon of six carbon atoms, with a hydrogen projecting out from each carbon at an angle of 120° to the bonds joining it to its carbon neighbors. Thus each carbon forms three obvious bonds, two with its neighboring carbons and one with the hydrogen; and yet the chemists are in the habit

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[6] R. S. Mulliken, Phys. Rev. 43, 279 (1933).

[7] E. Hückel, Z. Physik 70, 204 (1931); 72, 310 (1931); 76, 628 (1933).

[8] E. Hückel, Z. Physik 60, 423 (1930).

of thinking that carbon should form four bonds. Kekulé suggested many years ago that this could be explained if there were double bonds, say, between carbon atoms 1 and 2, between 3 and 4, and between 5 and 6, if we number them in order around the ring, but single bonds between 2 and 3, between 4 and 5, and between 6 and 1. This would involve us in a difficulty, however, for the internuclear distance in a double bond is known to be less than in a single bond, from many compounds where the bonding is unambiguous, and yet in the benzene molecule the distances are all the same. This was commonly explained, in terms of single and double bonds, by bringing in the alternative structure in which the double bonds were between atoms 2 and 3, 4 and 5, and 6 and 1, with single bonds between the others, and by assuming that somehow the actual structure was a compromise between these two possibilities.

In terms of the valence bond theory, which we shall describe in the next chapter, Pauling(9) explained this by assuming that each of the two possibilities represented an unperturbed wave function, and that the true wave function was a linear combination of the two; in this particular case, since the two states were degenerate, it would be a sum of the two, and on account of making the linear combination, the energy of the resulting ground state would be decreased by the amount of the non-diagonal matrix component between the two states. This process of combining the degenerate states was called resonance by Pauling, in analogy with Heisenberg's original use of the term resonance in discussing the interaction of two identical systems.(10) In this way Pauling's resonance theory of chemical binding grew up, as we shall describe more in detail in the next chapter.

Hückel, however, in the papers which we have quoted, proceeded in quite a different way, by using the ideas of molecular orbitals. Let us consider very briefly the symmetry properties of the molecular orbitals in a force field such as that of the benzene molecule. In the first place, the potential energy is symmetrical with respect to reflection in the plane of all the atoms. One can then deduce that all electronic wave functions must be either symmetrical or antisymmetrical under such a reflection. The electrons whose wave functions are symmetric are called σ-electrons, those with antisymmetric wave functions are π-electrons. A study, which we shall reserve for later, shows that the σ-electrons are responsible for the three ordinary bonds of which we have spoken, and there is nothing remarkable about them.

As for the π-electrons, each carbon atom by itself would have an atomic p-electron orbital whose wave function would have a nodal plane in the plane of the benzene atoms. The π-electron molecular orbitals are built up out of these atomic orbitals, if we wish to use the approximation of making linear combinations of atomic orbitals, as we did with H_2. Thus we have six atomic p functions, which of course will combine into six molecular orbitals. We realise that the six atoms in their ring are very much like a one-dimensional crystal of six

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[9] L. Pauling, J. Am. Chem. Soc. 53, 1367, 3225 (1931); 54, 988, 3570 (1932); Proc. Nat. Acad. Sci. 18, 293 (1932); J. Chem. Phys. 1, 280 (1933); L. Pauling and G. W. Wheland, J. Chem. Phys. 1, 362 (1933); and later papers.

[10] W. Heisenberg, Z. Physik 38, 411 (1926); 39, 499 (1926); 41, 239 (1927).

atoms, closed on itself; and Hückel used the analogy of the crystalline problem which had been worked out shortly before by Bloch.$^{(11)}$ to deduce the nature of the wave functions. If we label the atomic orbitals a_j, where j goes from 1 to 6, then the analogy with the metallic problem (which of course can equally well be directly deduced from group theory) tells us that the linear combinations of atomic orbitals having the correct symmetry to represent molecular orbitals are

$$\sum(j)\, e^{ikj} a_j\ .$$

where k is so chosen that the function is single-valued; that is, so that the coefficient e^{6ik}, which we get by putting in j = 6, is the same value that we should have had by putting in j = 0, which should equally well represent the sixth atom. In other words, we must have $e^{6ik} = 1$, or $6k = 2n\pi$, where n is an integer, or $k = n\pi/3$. There are just six independent values of k, which we may take to be 0, $\pi/3$, $2\pi/3$, π, $4\pi/3$, $5\pi/3$; the next value would be 2π, which yields nothing new. We note, however, that $e^{5\pi i/3}$ equals $e^{-\pi i/3}$, and $e^{-4\pi i/3}$ equals $e^{-2\pi i/3}$, so that we can equally well take k to have the values 0, $\pm\pi/3$, $\pm 2\pi/3$, π.

We have, then, six wave function, but obviously some degeneracy, for the two functions with $k = \pm\pi/3$ will obviously have the same energy, as will those with $k = \pm 2\pi/3$. The formula for energy is set up as in the metallic problem, as we shall show later when we come to a more detailed discussion of this case. We find that k = 0 corresponds to the lowest one-electron energy; this corresponds to the bottom of an energy band in a solid. The two states with $k = \pm\pi/3$ come next, then those with $k = \pm 2\pi/3$, and finally that with $k = \pi$, in which the successive coefficients e^{ikj} are ± 1, so that the wave function alternates in sign from one atom to the next, is the highest, and corresponds to the top of the energy band with a solid.

We next ask how many electrons we have in this energy band. Each carbon atom has two 1s electrons, two 2s, and two 2p, in the free state. When we come to examine the problem of the molecular orbitals more in detail, we shall find that all but one of these can be accomodated in the σ-type molecular orbitals, which we are not considering at the moment. This leaves us with one electron per atom for the π-electron orbitals, or six in all. Obviously we should expect that these would fill the three lowest states, with k = 0, $\pm\pi/3$, with two electrons each, one of each spin. This describes the structure which Hückel postulated for the benzene molecule, and one sees that, since each of these orbitals treats each of the six carbon atoms in an exactly equivalent way, we get away entirely from the difficulty of having to describe the molecule as having alternating single and double bonds. Essentially this type of description seems like certainly the correct way to look at this problem.

The papers of Hückel had a great effect in turning the direction of the workers in the field toward what are called unsaturated hydrocarbons. These are substances in which there are enough electrons to form a certain number of double bonds, but not as many as we could

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[11] F. Bloch, Z. Physik 52, 555 (1928).

imagine geometrically (as benzene may be considered to have three double bonds among the six bonds connecting carbon atoms). There are many chain compounds having this property, and in some cases some of the bonds, as judged by the internuclear distance, are close to double bonds, while others are close to single bonds, the internuclear distances showing an alternation. In other cases this alternation is not present. Compounds showing this sort of behavior are called conjugated compounds by the chemists. In a chain compound of this sort, we again have an analogy to a one-dimensional crystal, only now it is terminated at the ends, so that the boundary conditions are different from the cyclic boundary conditions in the ring compounds. Lennard-Jones(12) and his students, following this idea, showed that it was possible to get solutions for the energy levels of the molecular orbitals in such problems, and derived many results from the method, in agreement with experiment; the solution of the secular equations for the molecular orbitals actually yielded the sort of alternation observed. Work along the same lines has proceeded rather continuously since these early papers. Mulliken(13) and his coworkers have written considerably on it; and since the War it has been taken up again by many workers.(14)

Another line of research inspired by the work of Hückel concerns the excited energy levels of benzene and of the aromatic or ring compounds. In an important paper, Goeppert-Mayer and Sklar(15) applied molecular orbital methods to a calculation of excited energy levels of benzene. They used the general formulation of Hückel, but they went far beyond him in the general technique of handling the problem. Hückel had computed the one-electron energy of an electron in the field of six-fold symmetry representing the benzene molecule, and had got the energy levels in terms of certain exchange or resonance integrals, which he did not try to compute from first principles. He, and many succeeding users of the molecular orbital method, merely used these one-electron energies to represent the energy levels of the molecule, calling essentially on Koopmans' theorem to justify this (though not always recognizing this theorem by name). Goeppert-Mayer and Sklar, however, proceeded in a more fundamental way, setting up a determinantal function constructed out of the molecular orbitals, and setting about to compute the energy of the many-electron problem by averaging the Hamiltonian over this wave function. They could not carry this very far, for certain three-center integrals (which we shall later examine more in detail) were too difficult to compute properly. But they set a pattern for many later calculations, in which such determinantal many-electron functions are set up.

One rather remarkable line of work has resulted from this study of excited energy

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[12] J. E. Lennard-Jones, Proc. Roy. Soc. (London) A158, 280 (1937) and later papers.

[13] See for instance R. S. Mulliken and C. A. Rieke, J. Am. Chem. Soc. 63, 1770 (1941).

[14] See for instance C. A. Coulson and H. C. Longuet-Higgins, Proc. Roy. Soc. (London) A191, 39 (1947), and many later papers.

[15] M. Goeppert-Mayer and A. L. Sklar, J. Chem. Phys. 6, 645 (1938).

levels of aromatic compounds: an extensive set of papers on the colors of organic dyestuffs. This work more or less started with further papers by Sklar and Herzfeld(16) following fairly directly from the work on benzene. It has developed, however, along a rather different line. The reader familiar with the theory of metals will realize that the Bloch theory of energy bands often can be well approximated by the simpler Sommerfeld theory of free electrons. It occurred to a number of workers in the field that in a similar way the distribution of energy levels in the aromatic and unsaturated compounds might be approximated by thinking of the molecules as one-dimensional regions in which free electrons of a Sommerfeld type were free to move, with merely the quantum condition that there be a whole number of half wavelengths of the de Broglie waves in the length of the chain, or a whole number of wave lengths around a closed ring in a cyclic compound. We realize, of course, that there is a close resemblance between the two points of view in the study of metals, where the Bloch theory gives a distribution of energy levels much like what we should find with the Sommerfeld theory but with an effective mass rather than the true electronic mass, provided we are interested only in the distribution of levels at the bottom of the energy band. With this point of view, an extensive set of papers has grown up, relating to the behavior of the conjugated molecules, the absorption of light by dyestuffs, and so on, in which the workers in the field appear to find extensive agreement with experiment. The theories in this particular part of the subject may well be oversimplified; and yet one gets the impression that this type of approximation ought to be rather good, and that it may well be that much of the work along these lines may prove on closer examination to be a good first approximation.(17)

From the survey which we have given, it is clear that the method of molecular orbitals has found widespread application in chemical problems. Most of the work before the War was only semi-quantitative in character. Since the War, however, there has been a great burst of activity in the field, including much work of a quantitative degree of accuracy not attempted before. In this country, Mulliken(18) and his coworkers have initiated a program of numerical calculation of molecular orbitals, by a modification of the self-consistent field method using linear combinations of atomic orbitals, often abbreviated LCAO. They set up such linear combinations of atomic orbitals (like our combinations $a \pm b$ for the hydrogen problem) having the proper symmetry to represent molecular orbitals, and in most cases have enough atomic orbitals so that the coefficients of the LCAO's cannot be predicted uniquely from symmetry considerations alone, as they could in the hydrogen case. They then set up a determinantal

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[16] Various papers by A. L. Sklar and K. F. Herzfeld, 1937-1942.

[17] See papers by O. Schmidt, 1938-1940; R. Daudel, P. Daudel, A. Pullman, and B. Pullman 1945 to the present.

[18] See for instance R. S. Mulliken, J. Chem. Phys. 46, 497, 675 (1949); C. C. J. Roothaan, Revs. Modern Phys. 23, 69 (1951); R. G. Parr and B. L. Crawford, Jr., J. Chem. Phys. 16, 526, 1049 (1948); C. C. J. Roothaan and R. S. Mulliken, J. Chem. Phys. 16, 118 (1948); J. E. Mulligan, J. Chem. Phys. 19, 347 (1951); and numerous other papers.

wave function for the ground state of the molecule, made up out of these molecular orbitals expressed in terms of atomic orbitals. These determinantal wave functions of course involve the coefficients involved in the LCAO's, as yet undetermined. They compute the energy of the molecule from this determinantal wave function, and then vary the undetermined coefficients to make this energy a minimum. In this way they determine the final coefficients required to represent the molecular orbitals in terms of atomic orbitals, and from this can easily get the one-electron energies corresponding to the molecular orbitals. We see that if they had complete flexibility in the functions which they were varying, their procedure would be precisely that leading to the Hartree-Fock method. Since their LCAO's are not completely flexible functions, the results cannot be as good as those of a Hartree-Fock calculation, but nevertheless they represent a conscientious attempt to take the first really quantitative step toward a self-consistent treatment of molecules, and their results have shown very gratifying agreement with experiment.

In England as well the method of molecular orbitals is being developed at a very rapid rate at the present time. Extensive groups of papers in the last five years by Lennard-Jones, Coulson, Pople, Hall, Longuet-Higgins, Dewar, and a number of others have contributed greatly to our understanding of the method, and of its application to chemical problems. The literature is becoming so extensive that the reader is referred to the bibliography for the detailed references. More and more it is becoming clear that the method of molecular orbitals represents an approach to chemical problems which is more satisfactory than any other, and that as it becomes more and more quantitative, it can be hoped to lay a really exact foundation for chemical theory. We must remember one reservation, however. From the preceding chapter, we remember that the method of molecular orbitals does not lead to correct behavior at infinite internuclear distances, unless we take into account the configuration interaction with higher configurations; thus in the H_2 molecule we have to take into account not only the molecular orbital ground state, in which both electrons are in the symmetric orbital a + b, but also its configuration interaction with the excited state in which both electrons are in the antisymmetric orbital a - b, in order to get a correct description of the molecule at infinite separation. Such configuration interaction has not been taken into account in most of the work done by the molecular orbital method. It is probably not a very serious source of error, but nevertheless it must warn us that the method, as usually used, is only partially correct. Some beginnings in the direction of configuration interaction have been made, for instance, by Craig.(19) But they will have to be carried much further before we really have a satisfactory theory of molecular structure. In the next chapter, we shall take up in detail these questions of configuration interaction, and of the efforts to understand them being made in the Solid-State and Molecular Theory Group at M.I.T., where they form the main topic of

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[19] D. P. Craig, Proc. Roy. Soc. (London) A200, 474 (1950), and other papers.

interest.

3. Diatomic and Linear Triatomic Molecules

We have now followed the history of the development of the molecular orbital theory far enough so that we are ready to go into more details regarding it. Our main problem is that of finding the one-electron orbitals: given a potential function representing the potential of all nuclei, and all electrons but one, acting on the remaining electron in a molecule, how do we solve a one-electron Schrödinger equation for that electron? We cannot separate variables as with the atomic problem, solving the angular parts of the Schrödinger equation exactly by means of spherical harmonics, and being left only with a function of r to be determined by numerical integration. Nevertheless, the symmetry properties, which are the nearest analogue to the spherical symmetry of the single atom which we have left with a molecule, can often be a great help in the solution of the Schrödinger equation, and in this Section we shall consider those symmetry properties, as well as considering the problem of setting up wave functions of the proper symmetry. The symmetry properties can be most systematically handled by means of the group theory. Nevertheless most of the simpler cases can also be treated by elementary means, and we shall follow that method here, believing that after the reader has handled the problems by elementary methods, he will be able to understand the group theory treatments, such as that already quoted by Mulliken, more thoroughly, and will be less likely to make mistakes in its use. In our treatment, we shall use the method of handling a number of typical special cases, rather than of trying to build up a general theory.

First we consider diatomic molecules; they are the simplest, and were for a number of years the only case simple enough to treat, and they were the problem for which the method of molecular orbitals was really devised in the first place. Here, since the potential is unchanged if we rotate around the axis of the molecule, we can still carry out a separation of variables, though not as complete as with the spherically symmetrical problem. We can write the wave function as a product of a function of the angle of rotation about the axis, and a function of the two coordinates in a plane passing through the axis, and find at once that the function of the angle is a simple exponential, $e^{im\phi}$, if ϕ is the angle, or $\cos m\phi$ or $\sin m\phi$, where m is an integer. By analogy with the atomic case, we denote an orbital with $m = 0$ as a σ state, one with $m = \pm 1$ as a π state, $m = \pm 2$ a δ state, ± 3 a ϕ state, and so on (σ, π, δ, ϕ being the Greek equivalents of s, p, d, f). The two π states with ± 1 for m can be denoted π_+ and π_-, to distinguish them. If we are building up our molecular orbitals as linear combinations of atomic orbitals, it is obvious that we must use atomic orbitals with the same value of m as the corresponding molecular orbital. Thus in the case of hydrogen, as treated in the preceding chapter, we built up a σ molecular orbital out of atomic 1s orbitals. We could equally well have built up orbitals of the same symmetry out of atomic 2s orbitals. But we could also have used atomic 2p orbitals corresponding to $m = 0$. According to a commonly accepted notation for molecular orbitals, a σ orbital formed from atomic 2s functions would be called $2s\sigma$, and one from 2p orbitals a $2p\sigma$. On the other hand, we could build π orbitals out of the 2p atomic orbitals having $m = \pm 1$, and in that case we should call them $2p\pi$ orbitals. Extension of this notation to higher states is obvious.

In a homopolar molecule, one composed of two like atoms, there is a further requirement that the wave function be either symmetric or antisymmetric if we reflect in the midpoint of the line joining the atoms. A wave function which is even is denoted by the subscript g (for gerade), one which is odd by a subscript u (for ungerade). It is worthwhile asking at this point why we must have this symmetry or antisymmetry; we accepted it without question in the preceding chapter, but it is the simplest example of a type of symmetry which we shall find in many other cases, and we should understand its origin. Suppose we have a wave function which is neither symmetric nor antisymmetric with respect to reflection in the midpoint. On account of the symmetry of the potential function, the wave function which we get from the original function by reflection must also be an eigenfunction of the problem. Let the original function be u_1, the reflected function u_2. Also by symmetry the eigenvalue corresponding to u_2 must equal that for u_1. Hence we have a degenerate problem, and any linear combinations of u_1 and u_2 may be used as eigenfunctions as well as u_1 and u_2 themselves. Let us then build up the combinations $u_1 \pm u_2$. The first of these functions is symmetric, the second antisymmetric. Thus we have shown that if we start with a wave function which is neither symmetric nor antisymmetric, we must have two degenerate levels from which we can form a symmetric and an antisymmetric combination. It is then a self-contradictory assumption to suppose that we could have a non-degenerate state which was neither symmetric nor antisymmetric. Hence if we have a non-degenerate state, it must necessarily be either symmetric or antisymmetric; while if we have a degenerate state, we can make symmetric and antisymmetric functions from the two degenerate states. In either case, the final functions are symmetric or antisymmetric.

It is now clear, with a homopolar molecule, that from each atomic function on a single atom, we can build up a symmetric, and an antisymmetric, combination, just as in the preceding chapter we built up the combinations $a \pm b$. We may then build up a set of functions resembling molecular orbitals, in that each one depends on angle through the factor $e^{im\phi}$ and is either symmetric or antisymmetric under a reflection in the midpoint, by linear combinations of atomic orbitals. These functions of course will not be real molecular orbitals, for those are defined as real solutions of the self-consistent field problem. Nevertheless for qualitative work we may use them as molecular orbitals, as we did in the preceding chapter. If we wish more accurate approximations to molecular orbitals, we may make linear combinations of a number of these approximate functions. To make the best combinations, of course we compute the average energy of the combination, using the one-electron Hamiltonian derived from the self-consistent field problem, and vary the coefficients of the linear combination to make the energy stationary. As we know, this is equivalent to solving a secular equation between the various unperturbed functions, and for this secular equation we must compute the matrix components of energy between the unperturbed wave functions. We now find very easily that there will be no non-diagonal matrix components of energy between two functions with different m values or between an even and an odd function. Thus the secular equation factors, and we have separate problems for each m value, and for each symmetry. We thus see the advantage in picking out combinations of atomic orbitals having the proper symmetry behavior. The combinations of atomic orbitals having this proper symmetry are often called symmetry orbitals. In a later section we shall go much further into the details of the method of getting the best linear combinations of these symmetry orbitals to approximate the real molecular orbitals. We note that with a heteropolar molecule, consisting of two unlike atoms, we no longer have the symmetry property of the orbitals, so that our secular equation does not factor as completely as for the homopolar molecule.

Let us now consider a few specific molecules. We know surprisingly little about the exact details of the molecular orbitals for the diatomic molecules; in the last few years, when we have had the mathematical techniques for computing molecular orbitals fairly accurately, the interest has shifted to more complicated molecules, and for the simpler ones we still must use the rather early speculations made in the first days of molecular orbital theory. For H_2, as we have seen in Chapter 2, the lowest molecular orbital is the one which we might denote by $1s\sigma_g$, and the ground state of the molecule is that in which this orbital is occupied by two electrons (provided we disregard the configuration interaction with the state in which both electrons are in the state $1s\sigma_u$, as we are doing in this chapter). In the two helium atoms which would form a He_2 molecule if there were binding between them, two electrons are in the $1s\sigma_g$, two in $1s\sigma_u$, the total energy of the resulting combination being greater than for two separated atoms, so that there is no molecule formation. In Li_2, presumably the next molecular orbital energy level above the $1s\sigma_g$ and $1s\sigma_u$ is the one which we could denote as $2s\sigma_g$, and this is occupied by the two outer electrons of the molecule, giving a binding not unlike that in H_2. In Be_2, presumably the antisymmetric function $2s\sigma_u$ lies above the symmetric function $2p\sigma_g$, and the latter presumably is occupied by the outer two electrons, the former being empty. If instead we had the $2s\sigma_u$ occupied by two electrons, we could reasonably expect a repulsion, as between two helium atoms.

Let us next pass to N_2, O_2, and F_2, whose band spectra are well known, so that the order of their molecular orbital energies can be deduced with fair certainty. In these molecules, it seems likely that the order of energy levels, going from the most tightly bound, is approximately $1s\sigma_g$, $1s\sigma_u$, $2s\sigma_g$, $2s\sigma_u$, $2p\sigma_g$, $2p\pi_{\pm u}$, $2p\pi_{\pm g}$, $2p\sigma_u$. In N_2, with its fourteen electrons, the lower seven of these orbitals are filled with two electrons each; that is, they are filled through $2p\pi_{\pm u}$. This gives a ${}^1\Sigma_g$ state; each orbital is filled with two electrons, one of each spin, leading to the singlet; there are equal numbers of orbitals with positive and negative components of orbital angular momentum around the axis, so that it is a Σ state; and the number of u orbitals is even, so that when we reflect in the midpoint, the whole wave function does not change sign, and we have a g state. In O_2, the next two electrons go into the $2p\pi_{\pm g}$ states. There are two of these states, however, so that there are six possible configurations: two in which both electrons, one of each spin, are either in $2p_{+g}$ or $2p_{-g}$, and four in which one electron is in one orbital, one in the other. The first possibilities will lead to $^1\Delta$ states, the total orbital angular momentum being two units, whereas the last four, in the familiar way, will lead to a singlet and a triplet, in this case $^1\Sigma$ and $^3\Sigma$. As in an atom, the $^3\Sigma$ will lie below the $^1\Sigma$, and it proves to be the lowest state in the molecule; giving one of the few molecules with a triplet for a ground state, and explaining the paramagnetic nature of oxygen, arising on account of the magnetic moment associated with the spin. Careful consideration of the symmetry of the electronic wave function in this $^3\Sigma$ state shows that it is $^3\Sigma_g$, as we should expect. In F_2, the $2p\pi_{\pm g}$ states are filled, leaving only the $2p\sigma_u$ states unoccupied, and leading again to a $^1\Sigma$ state. Finally with two Ne atoms all these states are filled, and we have repulsion as with two heliums.

This gives us a good idea of the behavior of the molecular orbitals in homopolar diatomic molecules. In heteropolar molecules, we do not have the simplification introduced by the symmetry. Let us suppose that the two atoms are quite different in properties. Then the energy levels of the inner electrons in the two atoms will be quite different from each other. When we set up the two-center problem, there will still be wave functions and energy levels for these inner electrons, practically as in the isolated atoms. The wave function corresponding, say, to the 1s electron in the first atom will be very small in the neighborhood of the second atom, and vice versa. For the outer electrons, on the contrary, it may well be that the real wave functions will extend from one atom to the other. As a very simple example, suppose we were dealing with a molecule NaK. In Na_2, there would be a σ orbital formed from the 3s electrons on both Na atoms; these could combine to form symmetric and antisymmetric orbitals. We should certainly expect that in NaK there would be rather similar orbitals, but formed from the 3s electron of Na and the 4s of K. This suggests that in many cases it may happen that one atomic energy level of one atom, and another level of the other, may have approximately the same energy. Then the corresponding wave functions will become perturbed when the atoms form into molecules, and the resulting molecular orbitals will be combinations of the atomic wave functions of the two atoms, often with quite complicated properties. We shall give an example of this situation shortly, in the case of a triatomic molecule.

There is one property of the molecular orbitals in the heteropolar molecules which is quite different from what we find with the homopolar ones, and which has important consequences. On account of the lack of symmetry, each orbital will generally correspond to having different amounts of charge on the two atoms. In a symmetric or antisymmetric wave function, such as we have with the symmetric molecule, we necessarily have equal charges on each, but we have just seen that in the extreme case of an inner electron in a heteropolar molecule, the charge can be entirely concentrated in one atom, and we can have all intermediate cases between this situation and that of symmetrical charge distribution. Then when we build up a determinantal wave function out of these orbitals, adding the charge distributions in the various orbitals, we are by no means bound to come out with just enough electronic charge on each atom to balance its nuclear charge. According to our rules, we fill the lower orbitals with electrons, going far enough up to accomodate all electrons, and we may well leave the atoms with some degree of ionisation, though of course the total charge on the molecule as a whole will balance. This amount of ionization, plus on one atom and minus on the other, obviously does not have to be any integral multiple of an electronic charge, and the net dipole moment of the molecule which arises from it can have any value. There has been a certain amount of study of the dipole moments of diatomic molecules from this point of view; in general, the amount of ionization found on each atom is small, much smaller than naive ideas of the formation of the molecule from ions would suggest. There is room for much further study along the same lines.

Diatomic molecules are not the only ones having the type of symmetry of which we have been speaking in this section. It is obvious that any linear molecule will have the same quantization of the component of angular momentum along the axis, with the same σ, π, δ, and so on characterising its molecular orbitals. And any linear molecule with a center of symmetry will have the properties of having symmetric and antisymmetric orbitals. There are a number of important molecules falling into this class. For instance, among inorganic compounds, an important one is CO_2, which is a linear molecule with the arrangement OCO; among organic compounds there is acetylene C_2H_2, again a linear compound with the arrangement HCCH. Both of these compounds obviously are symmetrical about their midpoints, so that their orbitals are all either symmetric or antisymmetric with respect to inversion in this midpoint. A very thorough calculation of the molecular orbitals in CO_2 has recently been made by Mulligan,(20) and we shall discuss his results in moderate detail. This example will give us a chance to become somewhat acquainted with the LCAO, or linear combination of atomic orbital, method, which of course we have already discussed for H_2, but which underlies most of the recent work on molecular orbitals, and which we shall discuss more completely in a later section.

A carbon or oxygen atom has electrons in 1s, 2s, and 2p orbitals. On account of the threefold degeneracy of the 2p orbitals in an atom, there are five such orbitals for each atom. Out of these five atomic functions in the three atoms, we can construct fifteen linear combinations, which can represent approximations to the molecular orbitals. We could, if we chose, determine the fifteen molecular orbitals in the following fashion. We could set up the matrix components of a one-electron Hamiltonian operator between these functions, the operator consisting of the kinetic energy, and the potential energy in the self-consistent field of nuclei and all other electrons, determined for instance by the methods taken up in Chapter 1.

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[20] J. F. Mulligan, J. Chem. Phys. 19, 347 (1951).

We could then solve the resulting secular equation for the fifteen one-electron energies or eigenvalues of the problem, and for the eigenvectors or coefficients of the linear transformations expressing the correct wave functions as linear combinations of the original unperturbed functions. Thus we should find the molecular orbitals. The method used by Mulligan was slightly different, forming a direct analogy to the Hartree-Fock method, but the results will be very approximately the same by either scheme. We shall take up the relations between these two methods in a later section. For the moment let us merely consider Mulligan's results.

In the first place, we can simplify the problem greatly by introducing at the outset combinations of atomic orbitals having proper symmetry. The one-electron Hamiltonian will have no matrix components between two wave functions with different components of angular momentum along the axis; and it will have no matrix components between two functions one of which is symmetric and the other antisymmetric with respect to inversion in the midpoint. It is then very convenient to introduce linear combinations of the atomic orbitals, each characterized by a definite value of component of angular momentum along the axis, and each of which is symmetric or antisymmetric. Such a combination of atomic orbitals is often called a symmetry orbital. The secular equation will then automatically be factored, and will break down into a number of separate secular equations, one for each type of symmetry. Let us analyze this problem of CO_2 in detail, to see how many functions of each symmetry we shall have.

Each of the three atoms has three orbitals with zero component of angular momentum along the axis: the 1s, 2s, and 2pσ. Thus out of the nine functions of this type, we can construct nine σ orbitals of the molecule. Each atom has one orbital with + 1 component of angular momentum, and each has one with - 1 component. Thus there will be three π_+ orbitals, and three π_-'s. Within each type, we shall have orbitals symmetric and antisymmetric with respect to inversion, or of g and u type. Let us see how many of these we have. To do this, let us construct the symmetry orbitals. It is convenient to have some notation for the atomic orbitals, and we may as well use the notation employed by Mulligan. He refers to the 1s orbitals on the two oxygen atoms as o and o'; to the two 2s's on the oxygens as s and s'; to the 1s on the carbon as c, and to the 2s on the carbon as s_c. For the pσ's on the oxygens, he used the notation z and z', and for the pσ on the carbon, the notation z_c. The reason for this notation for the pσ's is the following. We take the z axis to be along the axis of the molecule, the oxygen atom with unprimed orbitals being found at negative z, the carbon atom at the origin, and the oxygen atom with primed orbitals at positive z. The 2pσ orbital then is written in spherical coordinates as having a factor $r \cos \theta$, where θ is the angle in polar coordinates. That is, for the carbon atom, this orbital has a factor z, with a nodal plane at $z = 0$, and positive values of the function for positive z, negative for negative. In a similar way the corresponding orbitals of the oxygens have nodal planes perpendicular to the z axes and passing through their nuclei, and in each case the atomic function is positive on the side of the nodal plane pointing along the direction of + z.

We can now see eaily that from our nine atomic σ orbitals, we can construct five symmetric or g functions, four antisymmetric or u functions. We may take the g symmetry orbitals as $o + o'$, $s + s'$, c, s_c, and $z - z'$. All of these are obvious except perhaps the last. The reason why we need the minus sign with the functions z and z' is that z is positive on the positive side of the nodal plane through the oxygen nucleus; that is, it is positive toward the carbon atom, negative away from it. For a g function, we must combine the corresponding function on the other oxygen which is positive toward the oxygen, but this function is negative toward increasing z's, and hence is $-z'$. In an analagous way, the u symmetry orbitals are $o - o'$, $s - s'$, $z + z'$, and z_c. Thus in our secular equation for the molecular orbitals, we shall have a fifth degree equation for the states of σ_g symmetry, and a fourth degree equation for those of σ_u symmetry. Mulligan simplifies by assuming, as is undoubtedly legitimate, that the 1s orbitals will not appreciably be mixed in with the 2s and 2p in making up the molecular orbitals. That is, he assumes that two of the σ_g molecular orbitals are identical with the symmetry orbitals $o + o'$ and c, and that one of the σ_u molecular orbitals is identical with $o - o'$. He then solves a cubic equation for the three linear combinations of $s + s'$, s_c, and $z - z'$ representing the three remaining orbitals of σ_g type, and another cubic equation for the three linear combinations of $s - s'$, $z + z'$, and z_c to form the three remaining σ_u orbitals.

The final linear combinations which Mulligan obtains, at the equilibrium distance of separation, are given in Table VII. As we see, he uses the notation $1\sigma_g$, $2\sigma_g$, etc., for the various resulting functions, the energies increasing as we go from $1\sigma_g$ to $2\sigma_g$, etc. From the values in the table, it is clear that we cannot identify any one of these orbitals with any one of the atoms; the corresponding atomic levels in the carbon and oxygen atoms are so nearly the same that we have combinations which are large on both. It is rather hard to interpret these functions without seeing them actually computed and plotted, and in Fig. 4 we give such a plot, though Mulligan does not give it. The thing which has been plotted is the value of the wave function at points along the line passing through the nuclei, computed from the formulas for the various atomic orbitals given in Mulligan's paper. To understand the figure, we must first remember the general form of the atomic orbitals. We remember that an atomic 2s function, like s, s', and s_c above, is finite at the nucleus, very rapidly decreases, goes through a node and changes sign, and has an outer part of considerable extent, of opposite sign to the value at the nucleus. The wave function actually is not as large in this

Table VII

$$1\sigma_g = 0.48(s + s') + 0.32s_c + 0.21(z - z'), \qquad 1\sigma_u = 0.38(s - s') + 0.11(z + z') - 0.51z_c$$

$$2\sigma_g = -0.51(s + s') + 0.40s_c + 0.46(z - z'), \qquad 2\sigma_u = 0.64(s - s') + 0.37(z + z') - 0.65z_c$$

$$3\sigma_g = 0.55(s + s') - 1.32s_c + 0.64(z - z'), \qquad 3\sigma_u = 0.85(s - s') + 0.84(z + z') + 1.55z_c$$

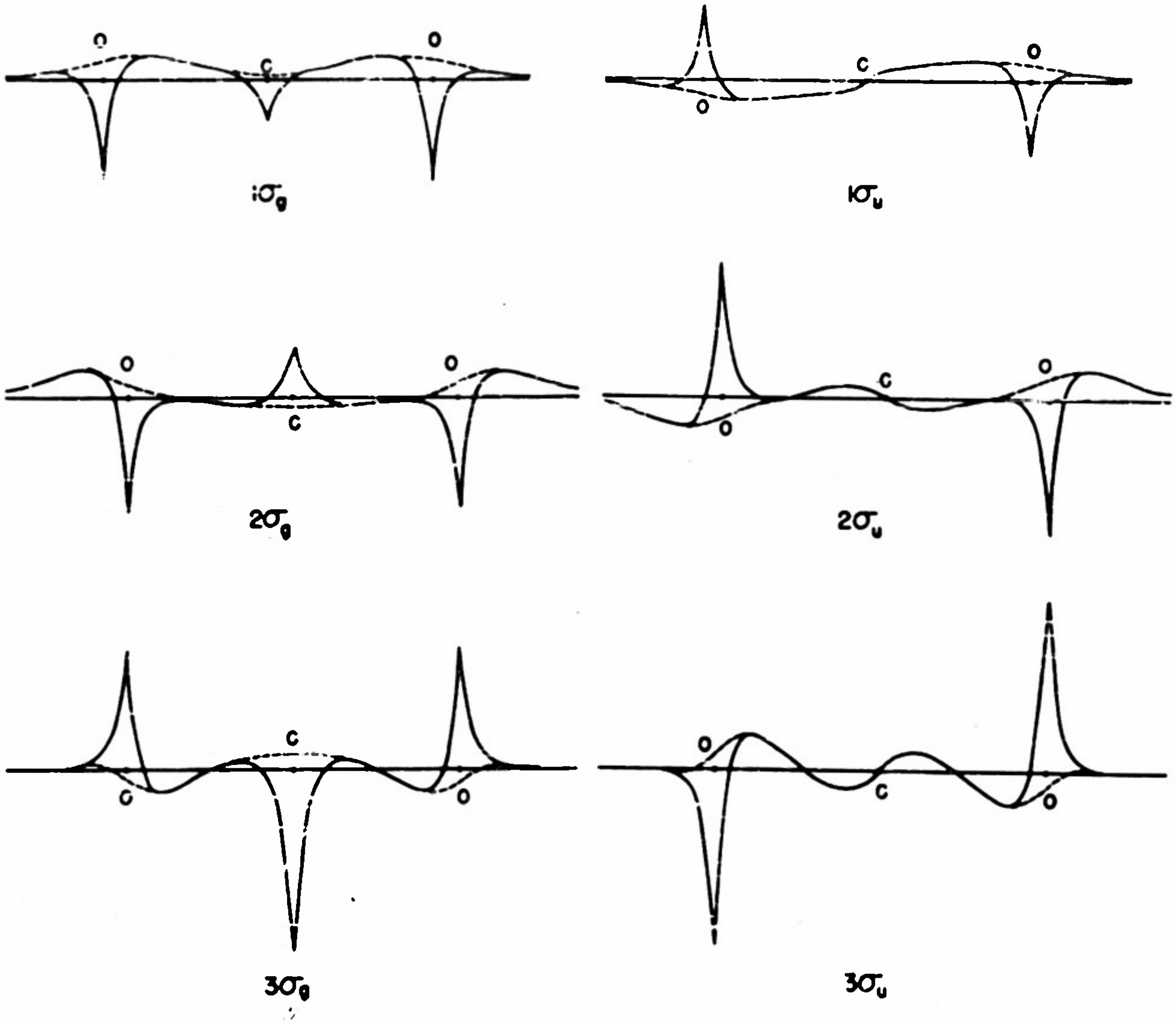

Fig. 4

Wave functions for states $1\sigma_g$ --- $3\sigma_u$ of CO_2, along internuclear axis, following Mulligan.

outer region as it is near the nucleus; but the volume of space near the nucleus is so small that only a small fraction of the charge is located near the nucleus, most of it being in the outer part of the wave function. Thus in Fig. 4 we clearly see the high peaks in the wave function near each nucleus, but we must remember that these are unimportant in considering the general behavior of the charge distribution.

To help the reader fix his attention on the important features of the wave function, we have drawn dotted lines in Fig. 4, showing the general trend of the wave functions if we disregard these peaks near the nucleus. Once we look at these dotted curves, we see what is going on: as we go from $1\sigma_g$ to $1\sigma_u$, $2\sigma_g$, $2\sigma_u$, and so on, we have a succession of curves each having one node more than the preceding one, and looking much like the successive wave functions of a one-dimensional linear oscillator, or like the successive sine curves representing the states of a one-dimensional particle in a box. The true nature of the wave functions, as we see in this way, is much like that of electrons freely wandering through the whole molecule. If we set up a cylindrical region about the size of the molecule, with a constant potential inside it, and a potential which rapidly rose outside the box, we should have wave functions for an electron in this cavity which would vary along the length of the cavity much like those which we have found, and which would fall off as we went out from the center of the cavity in a radial direction. Of course, in higher quantum numbers the wave function would also have nodes as we went out along the radius, but these would correspond to higher excitations than we are considering here. This sort of situation, in which the molecular orbitals have resemblance to the wave functions of a free electron in a cavity of the same size as the molecule, is of very widespread occurrence. Of course, the real wave function, as we see from Fig. 4, is modified near each nucleus, but this does not affect its general behavior.

There is an obvious resemblance between these wave functions and the sort found in a crystalline solid. We are familiar with the procedure of Bloch,(21) who superposed atomic orbitals to get one-electron functions in a crystal, showing that the resulting wave functions are similar to sinusoidal waves as found for a free electron. The present writer(22) has drawn curves for the wave functions of conduction electrons in metallic sodium, drawing dotted lines through the wave functions in just such a way as we have done in Fig. 4, and the similarity of those curves to these computed for CO_2 is quite striking. It is this similarity which makes it reasonable to approximate the behavior of electrons in aromatic and other compounds by replacing them by free electrons in a potential trough, as we discussed in the preceding section.

We have now considered the σ orbitals in the CO_2 problem in a good deal of detail; we shall next take up the π orbitals, though not going into them so thoroughly. We have a π_+ orbital on each of the atoms, so that as mentioned earlier, we can set up three π_+ molecular orbitals. The π_+ orbital on the carbon atom depends on r and θ through the factor $r \sin\theta$; that is, it is always positive, and has then the same value for equal positive and negative values of z, provided the angle ϕ is the same. Inversion through the origin can be thought of as made up of two operations: reflection in the plane $z = 0$, which does not change the value of the function, and rotation through 180° around the axis of the molecule, or increase of ϕ by 180°, which changes the sign of the factor $e^{i\phi}$ which appears in the wave function. Hence this function is of the u form, changing sign on an inversion. The sum of the two oxygen π_+ orbitals similarly has a u symmetry, and the difference has a g symmetry. Thus we have two u symmetry orbitals, and one g, made out of these π_+ atomic functions, so that the g function is uniquely determined without solving a secular equation, and we must solve a quadratic secular equation to find the two u's. We shall have another set of two u's and one g, determined from the π_-'s, degenerate with the first set. Mulligan has determined these functions, and expressed them in terms similar to those of Table VII.

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(21) F. Bloch, Z. Physik 52, 555 (1928).

(22) J. C. Slater, Revs. Modern Phys. 6, 209 (1934); see p. 247.

Now that we are familiar with the molecular orbitals, we can consider which ones are occupied in the ground state of the CO_2 molecule. Mulligan has found the one-electron energies of the orbitals, and his major interest is to compare these with observed energy levels as found in the band spectra; the argreement is quite good. For our present purposes, however, we care only about the order of the levels. The molecule has twenty-two electrons, six from the carbon, eight from each oxygen. The fifteen molecular orbitals would accomodate thirty electrons, so that the highest four orbitals, capable of holding eight electrons, must be unoccupied, and the remaining ones are those filled in making up the determinantal wave function. These highest four orbitals prove to be the $3\sigma_g$ and $3\sigma_u$ given in Table VII and Fig. 4, and the higher of the two π_u's formed from the π_+ and π_- atomic orbitals. Thus we understand exactly how to construct the molecular orbital wave function.

A great deal of thought has gone into the problem of how to estimate the nature of the molecular orbitals, and the value of their one-electron energies, in molecules of various types, without actually going through calculations such as Mulligan has made. We have noted in our historical survey that Mulliken and others for many years have been engaged in interpreting band spectra, with comparatively little use of detailed mathematical analysis. The methods used have mostly amounted to qualitative attempts to understand the nature of the wave functions, and to see what features of the wave functions are associated with bonding. Thus from H_2 we assume that a molecular orbital like the symmetric function a + b, which has a maximum in the region between the atoms, has a lower energy than an orbital like the antisymmetric function a - b, which has a node between the atoms. We can see why this should be so, in either of two ways. First, it is a general rule of wave mechanics that increasing the number of nodes increases the energy of the wave function, though this rule cannot be taken uncritically in any problem in more than one dimension. Secondly, the charge distribution between the nuclei in the symmetric function is in a region where the potential energy is lowered, on account of the fact that in this region both nuclei are attracting the electronic charge, and this lowers the energy of this state in comparison to the antisymmetric case, where charge is removed from this region between the atoms. In similar ways we can argue that the orbitals denoted as $1\sigma_g$ and $1\sigma_u$ in Fig. 4, which have large charge concentrations and no nodes between the carbon and oxygen atoms, should correspond to strong binding, and orbitals $3\sigma_g$ and $3\sigma_u$, which have nodes between the carbons and oxygens, should have high energy and discourage binding. Such qualitative arguments have been very useful, but as time goes on and we get more and more quantitative results like those of Mulligan, we shall no doubt have less need of such methods.

The chemists generally draw the CO_2 molecule by showing double bonds between the atoms, O=C=O, in order to satisfy their general rules that two bonds are to be attached to an oxygen atom, and four to a carbon. Mulligan undertook his study to see what would be meant by this double bond. It is clear that the actual situation is complicated. However, one feature that is definite in the structure is that both σ electrons and π electrons are included in the bonding process, and this seems to be a characteristic of a double bond. We shall see later that σ-type electron alone are concerned in single bonds, just as in hydrogen. On account of the way in which the wave functions are spread over the molecule, however, as shown in Fig. 4, it is rather clear that we cannot assign some of the electrons to the formation of bonds, and others to the separated atoms, in any such definite way as the chemists are accustomed to do.

4. Simple Planar Molecules -- Water and Ethylene

We have now become fairly familiar with the problem of the linear molecule, and shall go on to the next degree of complication, a molecule in a plane, using as illustrations two simple cases, water and ethylene. We first take water, a triangular molecule with the oxygen atom at the apex, the lines from oxygen to hydrogens making an angle of something over a right angle. For the sake of having the geometry definite, let us take the plane of the molecule to the yz plane, the z axis being the bisector of the angle between the two OH bonds, and the oxygen being at the origin. Then we note that there are a number of symmetry operations which can be applied to the molecule, leaving it unchanged. Thus we can reflect in the yz plane, or change x into - x; we can reflect in the xz plane, changing y into - y, so that one hydrogen changes into the other. We can rotate about the z axis through 180°, but this operation is not independent of the others; it is easy to show that successive reflections in the yz and the xz plane are equivalent to such a rotation. We may then reasonably expect that every molecular orbital will be symmetric or antisymmetric on reflection in the yz plane, and symmetric or antisymmetric on reflection in the xz plane.

We expect that there will be no degeneracy left in the molecular orbitals in this problem. Let us see why this is, in an elementary way. Let us suppose that we started with a fictitious problem in which the hydrogen atoms were brought into coincidence with each other and with the oxygen atom, so that all three nuclei were located at the origin. Then we ask what happens as we move the two hydrogen atoms, still coinciding with each other, away from the oxygen atom along the z direction, to form a diatomic molecule. Finally we separate the two hydrogens, moving one in the + y direction, the other in the - y direction, to form the triangular configuration of the actual molecule. The original combined molecule is identical with a neon atom, and has spherical symmetry, so that in th self-consistent field problem we have the degeneracy characteristic of the central field problem, and all states of the same l value, independent of their m, have the same energy. Thus in particular the three 2p orbitals all have the same energy. Now we move the two hydrogens, still coinciding with each other, along the z axis, to form a molecule which in fact would form an oxygen atom and a helium atom. We should now have the type of linear symmetry considered in the preceding section. All orbitals would have quantized angular momentum about the z axis. Out of the oxygen atomic orbitals we could construct symmetry orbitals of a σ and a π type. The π orbitals would have angular dependence of the form of $e^{\pm i\phi}$ with respect to rotation about the axis, and would be zero along the internuclear axis, while the σ orbitals would be independent of rotation, and would have their maximum values along the axis. Thus these two types of orbitals would have quite different energies, since the σ types are more concentrated in the region between the two atoms than the π types. We must realize that, since we are not dealing with a homopolar molecule, we shall not have g and u-type combinations, but nevertheless some orbitals will have nodal planes between the two atoms, and others will not, and the σ-type orbitals with no nodal planes will have lower energies, those with nodal planes will have higher energies, while the π-type orbitals will not be split so much in their energy.

We are still left with a certain amount of degeneracy with this linear molecule: with each π-type orbital we have two degenerate states corresponding to wave functions with factors $e^{\pm i\phi}$. We can also write these wave functions in a different way, more convenient for what will follow immediately. We can write the functions with factors $\cos\phi$ and $\sin\phi$, or what is the same thing, with factors x and y, giving nodal planes respectively as the yz and xz planes. That is, the first type of function is antisymmetric with respect to reflection in the yz plane, the second antisymmetric with respect to reflection in the xz plane, but each is symmetric with respect to reflection in the other plane. Now let us see what happens when the two hydrogen atoms are separated as in the actual molecule. It is clear that the effects on the π-like functions with nodal planes in the plane of the molecule, the yz plane, will be quite different from those with nodal planes in the xz plane; the former types of orbitals are zero at the positions of the hydrogen atoms, while the latter types have maxima here. Thus the degeneracy between the two types of functions which would be π-orbitals in the linear case is removed, and at the same time we see that by setting up our functions with nodal planes in the yz or xs planes, we automatically have got the correct sort to represent the symmetry of the final molecule.

It is perhaps worthwhile at this point to say something a little more profound about the requirement that our wave functions be symmetric or antisymmetric on reflection in the xz and yz planes, and that the degeneracy be removed; this is the sort of statement which we shall have to make in all the various types of symmetry which we shall meet, and while we shall not go into the group theory to prove the consequences of the symmetry in the matter of the behavior of the wave function, nevertheless we may as well begin to understand the fundamentals of symmetry operations. In the first place, an operation of reflection, or of rotation, is not in principle different from any other operation in quantum mechanics. To reflect in the yz plane, for instance, we have seen that we change x into $-x$. In other words, under this operation a given function of x, y, and z is changed into another function. The new function may be identical with the original function (if the original function is symmetric in x) or equal to its negative (if it is antisymmetric). More generally it might be a quite different function. If we have such an operator, which we may call R, we can let this operate on each wave function of a complete orthogonal set, and obtain in this way a set of functions Ru_1, Ru_2, . . . , where u_1, u_2, . . . formed the complete orthogonal set. These transformed functions may in turn be expanded in terms of the complete orthogonal set, so that we may find the matrix components of R, which are just the expansion coefficients: $Ru_i = \sum(j) R_{ji}u_j$. If R_{ji} is a diagonal matrix, the operation R transforms u_i into a constant times itself, and in the cases of symmetric and antisymmetric functions this constant is 1 and - 1 respectively. If R_{ji} is not diagonal, Ru_i must be written as a linear combination of more than one member of the complete orthogonal set.

Before we are through, we shall find examples of both diagonal and non-diagonal matrices for such operators, but our present simple case, where all functions are either symmetric or antisymmetric with respect to reflection both in the yz and the xz plane, is one where both these operations, which we may call R_{yz} and R_{xz}, simultaneously have diagonal matrices. We realize from our general knowledge of quantum mechanics that we cannot have two operators whose matrices are simultaneously diagonal unless two conditions are satisfied: first, each operator must commute with the energy, in order that its matrix may be diagonal with respect to functions which are eigenfunctions of the energy; secondly, the two operators must commute with each other. If the two operators both commuted with the energy, but did not commute with each other, we could make either one diagonal, but not both. We have met this situation before: in Chapter 1, we found that the x, y, and z components of angular momentum have operators each of which commutes with the energy, but which do not commute with each other. We then were able to diagonalize one of these operators, which we generally chose to be the z component of angular momentum, but could not diagonalize the others. The x and y components of angular momentum had non-diagonal matrix components, and yet they represented constant quantities, since they commuted with the energy. The way they achieved this was that there was degeneracy, and the x and y components had non-vanishing matrix components only between two degenerate states, whose time dependence therefore had zero frequency.

We now see that this situation can be perfectly general. If we have two symmetry operators, say R_1 and R_2, both of which commute with the energy, but which do not commute with each other, then we can choose eigenfunctions which will diagonalize both the energy and one of the operators, say R_1. But then R_2 cannot be diagonal, so that we must have degeneracy, and R_2 will have non-vanishing matrix components between the various degenerate states. This situation, then, of having non-commuting symmetry operators, necessarily leads to degeneracy. We shall later have more to say about why the angular momentum operators have these properties, so that we get the degeneracy in problems of rotational symmetry. For the moment, however, we are more interested in the simpler cases where all symmetry operators commute with each other as well as with the energy. For in this case, which we have with water, we can diagonalize each of the symmetry operators, so that each operator must transform the eigenfunction into a constant times itself, the constant in this simple case being either + 1 or - 1. As a result of this we have no degeneracy.

We must check, before we go further, that our two reflections R_{yz} and R_{xz} commute with each other and with the energy. In the first place, all the symmetry operators we shall consider commute with the energy; this is their fundamental characteristic. We can easily show that any symmetry operator which transforms the potential energy into itself will commute with the Hamiltonian. The reason is simple, as we can see from the case where the operation is transforming x into - x. We have in this case $Ru(x, y, z) = u(-x, y, z)$. Thus $HRu(x, y, z) = Hu(-x, y, z)$. But $RHu(x, y, z)$ is what we get when we transform x into - x in the function $Hu(x, y, z)$. We find x appearing in this function both through its appearance in u, and in H. In H it appears in the kinetic energy (where changing x into - x obviously makes no difference), and in the potential energy, where by hypothesis no change is to be made by the transformation. Thus the result is $Hu(-x, y, z)$, so that we see that $HRu = RHu$, or R and H commute with each other.

As for the other fact, that our two reflections commute with each other, this is almost obvious. The first operation changes x into - x; that is, it changes the first of the three arguments of u into its negative. The second changes the second of the three arguments of u into its negative. It is obvious that these operations can be applied in either order. We must be on our guard at this point, however: we shall find some operators before we are through which do not commute with each other, so that we must examine each case carefully.

We have now digressed long enough to examine the philosophy behind the symmetry of our orbitals in the case of water, and we may return to the very simple situation which we remember that we have here. First, all orbitals must be either symmetric or antisymmetric on reflection in the yz plane, the plane of the nuclei; second, all must be symmetric or antisymmetric on reflection in the xz plane, a reflection which carries one of the hydrogens into the other as to its mirror image. It is rather customary in such planar molecules to use a notation somewhat similar to that for linear molecules: the orbitals which are antisymmetric in reflection in the plane of the nuclei are often called π orbitals, and those which are symmetric are called σ orbitals. Let us now ask how orbitals of the required symmetry types can be built up as linear combinations of the atomic orbitals. We consider the 1s, 2s, and 2p atomic orbitals of oxygen, and the 1s of hydrogen.

We note in the first place that if we write the oxygen orbitals in the form of 1s, 2s, and $2p_x$, $2p_y$, $2p_z$, where $2p_x$, $2p_y$, $2p_z$ are of the form $xf(r)$, $yf(r)$, $zf(r)$, these orbitals already have the proper form for symmetry orbitals: each one is either symmetric or antisymmetric when x goes into - x, or y goes into - y. The two hydrogen 1s orbitals by themselves cannot serve as symmetry orbitals, however, for they are neither symmetric nor antisymmetric on reflection in the xz plane. Instead, we must make symmetric and antisymmetric linear combinations of them, just as we do in the hydrogen molecule: the sum represents the symmetric combination, the difference the antisymmetric. We thus have seven symmetry orbitals from which we can construct seven molecular orbitals. Of these, four, which are respectively 1s, 2s, $2p_z$, and the sum of the hydrogen orbitals, are even in both x and y; two, $2p_y$ and the difference of the hydrogen orbitals, are even in x, odd in y; and one, $2p_x$, is odd in x, even in y, and thus represents the only π orbital of the lot. None of these functions are odd in both x and y, though if we went to higher quantum numbers we should find functions of this sort. To find the molecular orbitals, we then must solve a biquadratic equation to get the orbitals even in x and y (though we may assume, as Mulligan did in CO_2, that the 1s by itself represents one of the orbitals, so that we need only solve a cubic for the three reamining ones). We must solve a quadratic to get the functions even in x, odd in y; and we already have the functions odd in x, even in y.

When we do this, we find that of the three orbitals formed from 2s, $2p_z$, and the sum of the hydrogen orbitals, the two of lower energy will both correspond to having considerable concentration of charge between the oxygen and the hydrogens, having some of the characteristics of the symmetric orbital a + b in the H_2 case, or the lowest orbitals in the CO_2 case as shown in Fig. 4. The highest energy of the three will go with an orbital which has nodes between the oxygen and the hydrogens. Similarly of the two functions formed from $2p_y$ and the difference of the hydrogens, the one of lower energy will have concentration of charge between oxygen and hydrogens, while the higher will have nodes. As for the π orbital, it has no considerable charge distribution near the hydrogens, and is unimportant as far as the binding is concerned. In the ground state of the molecule, where we have ten electrons to accomodate, eight from the oxygen and two from the hydrogens, we shall have two electrons each in the lower five of these orbitals; the empty ones will be those which, as we have just seen, have nodes between the oxygen and the hydrogens. The charge distribution corresponding to this determinantal function will then have concentrations between the oxygen and the hydrogens corresponding in a general way to the two bonds, but also there will be the concentration arising from the π electrons, extending in a direction perpendicular to the plane of the nuclei. This concentration in the π orbital becomes particularly important in the case of ethylene, which we shall take up next, and which in some ways resembles two water molecules placed adjacent to each other.

The ethylene molecule, C_2H_4, as we have just stated, is much like two water molecules in its shape. Along the z axis we may locate the two carbons, spaced at equal distances from the origin. The two hydrogens attached to each carbon are in a plane, which as with water we take to be the yz plane, stretching out in two triangles much like water molecules in shape and size. Our molecular orbitals, as with water, must be symmetrical or antisymmetrical on reflection in the yz and xz planes. Here, however, we have an additional symmetry operation, reflection in the xy plane, which brings one CH_2 group into the position formerly occupied by the other CH_2. Since these three reflections all represent operations which commute with each other, the molecular orbitals will be eigenfunctions for each operation, and they will be symmetric or antisymmetric when we carry out reflections in this xy plane.

To set up the symmetry orbitals, we can first proceed just as in water, setting up seven orbitals for each CH_2 group. For each, we have the carbon 1s, 2s, and $2p_z$, and the sum of the hydrogen 1s functions, giving four functions which are even on reflection in the yz and the xz planes; the carbon $2p_y$, and the difference of the two hydrogen 1s functions, giving two functions which are even on reflection in yz, but odd in xz; and the carbon $2p_x$, a π orbital, odd on reflection in yz, even in xz. None of these orbitals as they stand are either symmetric or antisymmetric on reflection in xy, but we can make sums and differences of the seven orbitals on the two CH_2 groups, so that each of the seven orbitals of each group generates two orbitals for the whole molecule, one even and the other odd on reflection in xy. We thus have fourteen orbitals, capable of holding twenty-eight electrons; but the molecule has only sixteen electrons, so that six of the fourteen orbitals must be empty in the molecular orbital representation of the ground state of the molecule. It is very important, then, to consider the order of the energies of the various orbitals, to see which ones are occupied.

In the first place, if the CH_2 groups were far enough apart so that they hardly interacted with each other at all, the final molecular orbitals, as well as the symmetry orbitals, would be very nearly the sums and differences of the symmetry orbitals on the two groups, and since the overlapping of the two would be very unimportant, the symmetric and antisymmetric orbitals generated from any single orbital of the CH_2 problem would have almost exactly the same energy. Thus we could expect that in this case the orbitals would resemble strongly those which we have described for water, supplemented by their mirror image (with or without change of sign) on the other group. As with water, we should expect that the two highest symmetric orbitals, and the two highest antisymmetric ones, would resemble the two which are unoccupied in water, having nodes between the carbon and the hydrogens. This would leave five orbitals which are symmetric in the xy plane, and five which are antisymmetric, capable of accomodating twenty electrons. When the CH_2 groups come closer together, however, each of the orbitals which is antisymmetric on reflection in the xy plane has a node between the two carbons, while the symmetric orbitals do not. Thus we may reasonably expect a considerable splitting of those orbitals whose wave functions overlap considerably in the region between the carbons, the symmetric orbital having its energy lowered, the antisymmetric ones having the energy raised.

There are two orbitals out of each CH_2 group which have this property of having considerable density between the carbons. Going back to the problem of water, we remember that the five occupied orbitals had the following behavior: one was essentially the oxygen (or in this case the carbon) 1s orbital; a second and third were combinations of the 2s, $2p_z$, and the sum of the hydrogen orbitals; the fourth was a combination of the oxygen $2p_y$ and the difference of the hydrogens; the fifth was the $2p_x$, a π orbital. When we examine the actual charge density in these orbitals, we find of course that the 1s is concentrated near the nucleus, so that these orbitals will not overlap or interact. Of the two combinations of the 2s, $2p_z$, and the sum of the hydrogens, one has a charge concentration which is largely located between the oxygen (or carbon) and the hydrogens, and is largely responsible for the oxygen-hydrogen binding. The other is rather small between the oxygen and hydrogen, having a nodal surface, and is large on the side of the oxygen away from the hydrogens. That is, this orbital is one of those which, in the ethylene molecule, will have large concentration between the carbons. Thus we expect that in ethylene the symmetric combination of these orbitals will correspond to a binding effect between the two carbons, while the antisymmetric combination will have a much higher energy, and will be unoccupied in the molecule. Next we come to the combination of the carbon $2p_y$ and the difference of the hydrogens. This has a concentration which is largely between the carbons and the hydrogens, so that it contributes to the carbon-hydrogen binding, and has small charge density between the carbons. Both the symmetric and antisymmetric combinations of these orbitals on the two CH_2 groups will then have about the same energy, though the antisymmetric orbital will lie somewhat higher, and both will be occupied in the ethylene molecule. Finally the π electrons are not shared with the hydrogens, forming molecular orbitals by themselves. Thus they will extend to a considerable extent toward the other carbon, and their symmetric combination will correspond to a considerable binding effect, and will be occupied in the molecule, while their antisymmetric combination will have a much higher energy, and will be unoccupied.

We have thus identified the orbitals which are occupied in the completed molecule. We see that in water there are two orbitals, one of σ type and one of π type, which do not take part in the binding with the hydrogens, but which are located so that the corresponding orbitals in ethylene can extend from one carbon toward the other. In water each of these orbitals is occupied by two electrons. Such pairs, not contributing to binding, have been called lone pairs by Lennard-Jones. In the ethylene molecule, the orbitals corresponding to these lone-pair electrons combine into a symmetric, binding combination, and an antisymmetric combination of much higher energy. The lower, binding orbital is occupied by two electrons in each case, while the higher orbitals is empty, consistent with the fact that ethylene has four fewer electrons than two water molecules. The two lone pairs, so to speak, are shared between two carbons.

According to the language of the chemists, there is a double bond between the two carbons in ethylene, and since the time of G. N. Lewis such a double bond has been identified with two pairs of electrons. We now see that this corresponds closely to the facts. One of the double bonds is formed from an orbital of the σ type, one of the π type, and this seems to be a general characteristic of double bonds. There is now a very important experimental fact about this double bond in ethylene, and in other cases: it does not show the property of free rotation. Ethane, C_2H_6, differs from ethylene in that ethane has a single bond between the carbons, and the three hydrogens are located in a triangle in a plane normal to the C-C axis, on the far side of the carbon from the other CH_3 group, so that the three hydrogens and the one carbon surrounding each carbon form approximately a regular tetrahedron. It is now found that in ethane either triangular set of hydrogens is very free to spin around the axis of the molecule; there is only a very slight tendency for the two groups of hydrogens to take up a definite orientation with respect to each other, and this tendency is thought to arise from the interactions between hydrogens on the two CH_3 groups, a very small interaction on account of the large distance. In ethylene, however, the situation is completely different. The molecule definitely wants to form a planar configuration. An attempt to rotate one of the sets of two hydrogens with respect to the other two, around the axis of the molecule, meets a very considerable restoring force, as one can find from band spectra, where the frequency of such twisting oscillations can be observed. The obstacle to the turning is much more than can be explained from any hydrogen-hydrogen interaction; there must be something in the double bond itself which opposes this rotation.

This feature of the double bond was brought out in the first treatment of the ethylene molecule and of the double bond, by Hückel.(23) In this paper, one of the first dealing with polyatomic molecules by the molecular orbital method, Hückel set up the molecular orbitals much as we have done, and fixed his attention particularly on the π orbitals. We shall find later that these are the ones missing in ethane: the single bond in ethane is much like that formed from σ orbitals in ethylene. The π orbitals in each of the two CH_2 groups have their greatest intensity along a line perpendicular to the plane of the molecule. Now if the molecule is twisted, of course we lose the planar symmetry; but in a very crude way we can say that each of the CH_2 groups would carry its π orbitals with it as the two groups were twisted with respect to each other. When the molecule is not twisted, the π orbitals on the two groups point in the same direction, and can overlap to a maximum extent. This overlapping of course does not occur on the line joining the carbons, for the π electrons have a node there; it occurs in two regions, one above and one below the plane of the molecule. Once the molecule is twisted, however, the regions of the maximum amplitude of the π electrons of the two groups no longer are found to overlap as much as before, and the overlapping is reduced. We assume that this overlapping is what is responsible for the reduction in energy of the symmetric orbital, and the increase in energy of the antisymmetric one; in other words, for the tightness of binding. We shall later have definite verification of this, when we begin to consider the calculations of the energies of orbitals. Thus we see, following Hückel, that twisting the molecule will make a considerable increase in energy, and we understand the stiffness of the double bond in opposing rotation. This explanation was one of the first real successes of the theory of the chemical bond, and later more quantitative calculations have borne out the correctness of Hückel's interpretation.

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[23] E. Hückel, Z. Physik 60, 423 (1930).

5. The Benzene Molecule

We have already quoted, in Section 2, the papers on the benzene molecule which Hückel wrote soon after he considered the ethylene molecule and the nature of the double bond. Let us now go a good deal more deeply into this problem, for it is a very informing one in many ways. In the first place, like water and ethylene, it is a planar molecule, so that one symmetry operation corresponds to reflection in the plane of the molecule. Now, however, in contrast to previous cases, we have a large number of symmetry operations, which do not all commute with each other, so that we must look for degenerate wave functions. Before going further, let us make a complete analysis of these symmetry operations, so that we can tell what to expect of the behavior of the orbitals

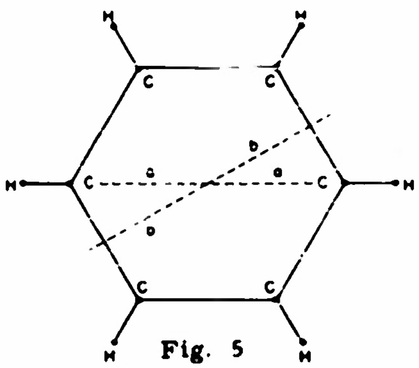

Fig. 5

We give in Fig. 5 a diagram of the molecule. Let us now list all the operations we can think of which will carry it into itself, aside from the reflection in the plane of the molecule which we have already mentioned. In the first place, we can rotate the whole figure about its center, by 60°, or any integral multiple of 60°. Six successive rotations through 60° bring the molecule back to its original position, or correspond, as one says in group theory, to the identity operation. It is a characteristic of the symmetry operations which we meet that a sufficient number of repetitions of one operation will always correspond to the identity operation; this is a necessary requirement of a group of operations. We have not pointed it out, but two successive reflections in the same plane correspond to the identity operation, so that the reflections, the only operations we have considered so far, fit in with this rule. In addition to the rotations, however, there are many other symmetry operations which bring the benzene molecule into coincidence with itself. Thus we can reflect in a plane perpendicular to the plane of the molecule, passing through two diametrically opposite carbons, like the plane intersecting the plane of the paper in the line aa in Fig. 5. We can also reflect in a plane cutting midway between opposite pairs of carbons, like that intersecting the plane of the paper in the line bb in Fig. 5. Finally we can rotate through 180° about any of the three axes like aa, or any of the three axes like bb. One such rotation, however, is equivalent to successive reflections in the plane perpendicular to the paper, passing through the appropriate axis, and reflection in the plane of the paper, just as we have already found in the case of water, so that it does not represent an independent symmetry operation. The operations which we have already mentioned include all the independent ones which we have with the symmetry of the benzene molecule.

Let us now examine which of our operations commute with each other. In the first place, the rotations of 60° and multiples of it about the axis perpendicular to the plane of the molecule all commute with each other: a rotation first through 60°, followed by one through

120°, for instance, is clearly equivalent to one through 120°, followed by one through 60°. If these rotations were the only symmetry operations which we had, then, we could diagonalize them all at the same time, and in the actual case we are allowed to do so, but not required to. Let us consider the consequences of diagonalizing them. The effect of rotating through 60° would be to multiply each wave function by a constant, which we may call α; this is the diagonal component of the matrix representing the operation. Now rotation through 120° is equivalent to two successive rotations through 60°, so that it must multiply the wave function by α^2. Continuing in this way, we see that rotation through 360° must multiply by α^6. On the other hand, we have already seen that this is the identity operation: rotation through 360° really changes nothing, and hence must leave the wave function unchanged, or must multiply it by unity. Hence we see that α^6 must equal unity, or that the only possible eigenvalues α for the rotation operation must be sixth roots of unity. There are six such sixth roots, which may be written in the form $\alpha = e^{m\pi i/3}$, where $m = 1, 2, 3, 4, 5, 6$. We shall make further use of these values of α a little later.

Before we go further, we may generalize a little the argument we have just used, and see that it applies in other cases as well. Whenever the successive application of the same operation n times gives the identity operation, then it is clear that if this operation has a diagonal matrix, the diagonal matrix components, or eigenvalues of the operator, must be one of the n n^{th} roots of unity. We may apply this principle to one example which we have already met several times. We have accepted, so far without proof, the fact that if a reflection in a plane has a diagonal matrix, the diagonal matrix components must be 1 or - 1; that is, the wave function must be symmetric or antisymmetric with respect to this reflection. We now see that this furnishes the simplest illustration of the general rule which we have just stated. For it is clear that two successive reflections in the plane are equivalent to an identity operation, so that we have the case where $n = 2$, and the two possible eigenvalues of the reflection operation are the two square roots of unity, 1 and - 1.

Now let us consider our reflection operations, and see if they commute with the rotations, and with each other. First, it is obvious that the reflections do not commute with the rotations. We may easily see this either by a diagram or analytically. Thus analytically we may investigate the effect of successive rotation through an angle θ, and reflection in the x axis, by writing the coordinates of a point in polar coordinates. Let us start with the point of coordinates R, ϕ. First rotate through θ; the coordinates go to R, $(\phi + \theta)$. Then reflect in the x axis, and the coordinates go to R, $(-\phi - \theta)$. Now we perform the operations in the reverse order. Starting again with R, ϕ, we first reflect in the x axis, going to R, $-\phi$. Then we rotate through θ, going to R, $(-\phi + \theta)$. It is clear that this is different from the result of the first operation.

In a similar way, we can see that reflections in two different planes will not in general commute with each other. Thus let us start with a point of coordinates R, ϕ, and reflect first in the x axis, then in a plane making an angle θ with the x axis. The reflection in the x axis changes the point to R, $(-\phi)$. Reflection in the plane making an angle θ with the x axis changes it to the point R, $(\phi + 2\theta)$, this angle being as much greater than θ as the former angle $-\phi$ was less than θ. Let us now reverse the order of the operations. Again we start with R, ϕ, but first reflect in the plane making an angle θ with the x axis. The point is changed to R, $(-\phi + 2\theta)$. Now we reflect in the x axis, changing the point to R, $(\phi - 2\theta)$. In other words, reflection in the two planes making an angle of θ with each other has had the same effect as rotating through an angle 2θ, in a direction pointing from the first plane toward the second. The two operations obviously do not commute with each other, except in one special case: if $\theta = 90^\circ$, so that $2\theta = 180^\circ$, then they do commute, for rotation through 180° is equivalent to rotation through -180°. This explains why in our earlier problems we found reflections in two planes at right angles to commute with each other; but that represents the only case in which two successive reflections commute.

There is another observation which we can make in our present case, however. All reflection planes make angles of 30° or multiples of 30° with each other. Thus any two successive reflections in different planes are equivalent to rotations through 60° or multiples of 60°, or are equivalent to the rotation operations which we have already considered. Then any even number of reflections are equivalent to rotations already considered, and any odd number of reflections are equivalent to a single reflection, plus a rotation of the type already considered. We can then generate all our symmetry operations from rotations and a single reflection. But we have already seen that reflection in a plane making an angle θ with the x axis changes the point R, ϕ to the point R, $(-\phi + 2\theta)$. Since all the reflection planes make angles of multiples of 30° with the x axis, we see that this is equivalent to a reflection in the x axis, plus a rotation through a multiple of 60°. Therefore finally we conclude that the rotations of multiples of 60° about the axis normal to the plane of the molecule, which we take to be the z axis, plus reflections in the xz plane, are capable of representing all possible symmetry operations.

We are now ready to examine the consequences of the non-commutability of the rotations with the reflection in the xz plane. We have a choice: we may diagonalize the rotation operations, in which case the reflection will not be diagonalized; or we may diagonalize the reflection, and not the rotations. In either case, by the general principles which we have examined before, we see that we must have a degeneracy. Thus if we diagonalize the rotation operations, the reflection operation must transform each wave function into another wave function, or a combination of others, but since the reflection operation commutes with the Hamiltonian, these other wave functions must correspond to the same energy values as the original one, so that we have degeneracy. We can understand the situation much better by seeing how the wave functions are described, in detail.

Let us first consider the case in which we diagonalize the rotations. Then we have already seen that rotation through 60°, or through the angle $\pi/3$, must multiply the wave function by one of the six eigenvalues $e^{im(\pi/3)}$, where $m = 1 \ldots 6$. In other words, the wave function behaves under a rotation exactly like the function $e^{im\phi}$. We can be more precise than this. Let us consider the behavior of the wave function in cylindrical coordinates, r, ϕ, z. Then rotation through an angle $\phi = \pi/3$, keeping r and z constant, will multiply the function by $e^{im\pi/3}$. This is consistent only with the assumption that the wave function itself is a product of a factor $e^{im\phi}$, by a function which is periodic with period $\pi/3$ on rotation. This is a special case of Floquet's theorem, whose use in the theory of energy bands in crystals is familiar to the solid-state theorist. We may then write $u(r, \phi, z) = e^{im\phi} v_m(r, \phi, z)$, where $v(r, \phi + \pi/3, z) = v(r, \phi, z)$.

Now let us inquire regarding the effect of a reflection in the xz plane, on such a wave function. We start with the six wave functions corresponding to m = 1, 2, 3, 4, 5, 6. When we reflect in the xz plane, the function $e^{im\phi} v_m(r, \phi, z)$ goes into $e^{-im\phi} v_m(r, -\phi, z)$. This must be expressible as a linear combination of the original six functions, and the coefficients of this combination represent the matrix components of the reflection operation. Now we note that when we rotate through $\pi/3$, our function $e^{-im\phi} v_m(r, -\phi, z)$ is multiplied by the factor $e^{-im\pi/3}$. This factor, however, equals $e^{i(6-m)\pi/3}$, which is just the original factor multiplied by $e^{2\pi i} = 1$. In other words, the function which we get by letting the reflection operate on the function with a given m transforms into a new function which behaves under a translation like the function whose index is 6 - m. Since we have only one function which transforms in this way, our rotated function must equal a constant times the function corresponding to 6 - m. We find, in other words, that the function with a given value of m, and with the value equal to 6 - m, are degenerate with each other. To be specific, the functions with m = 1 and 5 are degenerate, and those with 2 and 4 are degenerate.

These relations become easier to understand if we note multiplication by the factor $e^{i(6-m)\pi/3}$ is equivalent to multiplication by $e^{-im\pi/3}$, as has been mentioned earlier. Thus we could from the beginning have denoted our six states by the values m = 0, ± 1, ± 2, 3. Rotation through $\pi/3$ leaves the function with m = 0 unchanged; multiplies those with m = ± 1, ± 2 by $e^{\pm i\pi/3}$, $e^{\pm 2i\pi/3}$; and multiplies that with m = 3 by - 1. Then our statement regarding energies is that the states with equal positive and negative values of m are degenerate with each other, a very natural result. We have, then, four distinct energy levels, for m = 0, 1, 2, 3, out of our set of six functions, the states with m = 1, 2 being two-fold degenerate.

We should now expect that we could choose our functions as linear combinations of the six which diagonalize the rotations, in such a way as to diagonalize the reflections in the xz plane. In making these linear combinations, we are allowed of course only to combine states which are degenerate with each other, for only in this way will we still have eigenfunctions of the energy. Since there is only one state with m = 0, and only one with m = 3, these functions themselves must be eigenfunctions for the reflection. In other words, they must transform into themselves, or into the negative of themselves, under a reflection in the xz plane, or they must be symmetric or antisymmetric functions with respect to a transformation of y into - y. We have two states however, with m = ± 1, and two with m = ± 2, and we must be able to set up linear combinations of these which are eigenfunctions of the reflection. Putting it another way, we see that we can write the functions corresponding to $m = \pm 1$, or $m = \pm 2$, in the case where we are diagonalizing the rotations, as linear combinations of one function symmetric in y, and another antisymmetric in y.

We now know enough about the symmetry properties of our wave functions so that we can start constructing symmetry orbitals out of the carbon and hydrogen atomic orbitals in the benzene problem. Let us start with the simplest case, the 1s atomic orbitals of the carbon atoms. Let us number the carbons by an index j, $j = 1$ corresponding to that which is at an angle $\pi/3$ to the x axis, $j = 2$ to that which is at an angle $2\pi/3$, and so on, up to $j = 6$, which is on the x axis. We may then denote the 1s orbitals of the atoms as $s_1, s_2 \ldots s_6$. Now let us make the linear combination

$$u_m = \sum(j)\, e^{imj\pi/3}\, s_j . \qquad (3.1)$$

We shall now show that this combination has all the proper characteristics to make it a symmetry orbital. In the first place, we ask what happens to it when we rotate through $\pi/3$, or when we change the angle ϕ into $\phi + \pi/3$. This of course transforms $s_j(r, \phi, z)$ into $s_j(r, \phi + \pi/3, z)$. That is, we are now looking at the 1s function s_j on the jth atom, not at the point r, ϕ, z, but at a point rotated through $\pi/3$ with respect to this point. But this is equal to the value of the function s_{j-1} at the position r, ϕ, z. In other words, the operation of rotating through $\pi/3$ transforms $u_m(r, \phi, z)$, as given in (3.1), into

$$u_m(r, \phi + \pi/3, z) = \sum(j)\, e^{imj\pi/3}\, s_{j-1}(r, \phi, z) .$$

But by changing the name of the index of summation, this may be transformed at once into

$$u_m(r, \phi + \pi/3, z) = \sum(j)\, e^{im(j+1)\pi/3}\, s_j(r, \phi, z) = e^{im\pi/3}\, u_m(r, \phi, z) . \qquad (3.2)$$

From Eq. (3.2), we see that the function (3.1) transforms under a rotation as our functions should if they are set up to diagonalize the rotations.

We may next check the fact that our function (3.1) transforms properly under a reflection in the xz plane. For $m = 0$, we have the sum of the 1s functions on all carbon atoms, a function which is clearly symmetric on reflection. For $m = 3$, we have the sum of 1s functions with alternating signs, a function which again is symmetric on reflection. For $m = \pm 1$, our function may be rewritten in the form

$$u_{\pm 1} = \left\{ s_6 + \frac{1}{2}(s_1 + s_5 - s_2 - s_4) - s_3 \right\} \pm 0.866i(s_1 - s_5 + s_2 - s_4) , \qquad (3.3)$$

where $1/2 = \cos \pi/3$, $0.866 = \sin \pi/3$. Now the functions s_1 and s_5 are the reflections of each other in the xz plane, and s_2 and s_4 are reflections of each other. Thus we see that the first term in Eq. (3.3) is symmetric on reflection in the xz plane, and the second is antisymmetric, so that we have shown how to write our functions for m = ± 1 as a sum of symmetric and antisymmetric functions. These symmetric and antisymmetric functions are themselves the eigenfunctions of the reflection, in case we choose to diagonalize the reflection rather than the rotations. We note that these functions also diagonalize the reflection in the yz plane, which interchanges s_1 and s_2, s_4 and s_5, and s_3 and s_6. The first term of (3. 3) is antisymmetric in this reflection, the second symmetric. It is of course to be expected that a wave function which diagonalizes the reflection in the xz plane will also diagonalize that in the yz plane, since these two reflections commute with each other.

In a similar way, the functions for m = ± 2 can be rewritten in the form

$$u_{\pm 2} = \left\{s_6 - \frac{1}{2}(s_1 + s_4 + s_2 + s_5) + s_3\right\} \pm 0.866i(s_1 - s_2 + s_4 - s_5) . \qquad (3.4)$$

Here again the first term is symmetric, the second antisymmetric, on reflection in the xz plane; but now the first is also symmetric, and the second antisymmetric, on reflection in xy. It is now an interesting thing to observe that the two functions, one symmetric and the other antisymmetric in xz, appearing in (3. 3), are degenerate with each other, though they are of quite different appearance: that is, the two functions $s_6 + 1/2(s_1 + s_5 - s_2 - s_4) - s_3$ must have the same diagonal energy as $0.866(s_1 - s_5 + s_2 - s_4)$, and similarly the two functions of Eq. (3. 4) must have the same energy. In these functions, and all which we have written so far, we should point out that we have not yet normalized the functions, and of course this must be done before we can properly compute the matrix component of the energy or of other operators.

We have now shown how to set up six symmetry orbitals out of the carbon 1s atomic orbitals. Since these orbitals diagonalize the symmetry operations which commute with the energy, there will be no non-diagonal matrix components of energy between them, so that use of them will help in factoring the secular equation, as in the previous problems. We shall later consider the solution of this secular equation, so as to find the energy levels, but even before doing so, we can use our general knowledge of the behavior of wave functions to deduce the order of the one-electron energies. The function for m = 0 is simply the sum of the functions on the various carbons. Thus it will have no nodes, will correspond to a piling up of charge density between the atoms, and may be expected to have the lowest one-electron energy. At the other extreme, the function for m = 3 will have a node between each pair of atoms, and so may be expected to have the highest energy. This state for m = 3 may be considered to have three nodal planes, making angles of 30°, 90°, and 150° with the x axis. The states for m = 1, as we see from Eq. (3. 3), may be considered to have one nodal plane. It is convenient, for consideration of these nodes, to use the real and imaginary parts of (3. 3), or the functions which diagonalize the reflections, since the functions which diagonalize the rotations are complex, and do not have nodal planes. Then we see that the real part of (3. 3), which is symmetric in y, has the yz plane as a nodal plane, and the imaginary part has the xz plane as a nodal plane. In a similar way, the states for m = ± 2, from Eq. (3. 4), have two nodal planes. Thus the real part of (3.4) may be considered to have the 45° planes $x = \pm y$ as nodal planes, and the imaginary part has the xy and xz planes as nodal planes. We expect, then, that as the energy will increase with the number of nodal planes, the states for $m = 1$ will have the next lowest energy, and those with $m = 2$ will have the next highest energy.

In addition to the symmetry orbitals formed from the carbon 1s atomic orbitals, we have several other sets which behave just like these in the matter of symmetry. Obviously the carbon 2s orbitals will behave the same way, and so will the hydrogen 1s's. As far as the carbon 2p's are concerned, we must first consider how to remove the degeneracy of the atomic functions. We have not so far discussed the symmetry of the molecule arising from reflection in the plane of the molecule, or the xy plane, but we convince ourselves easily that this reflection commutes with all other symmetry operations, so that it will be diagonalized. In other words, all symmetry or molecular orbitals will be either even or odd on reflection in this plane, and as with the earlier cases, we call the even orbitals σ orbitals, and the odd ones π orbitals. Clearly, then, we wish to set up carbon 2p orbitals which are either of the σ type or π type, and the $2p_z$ will be of the π type. The six $2p_z$ orbitals on the six carbons have the same symmetry properties, as far as all the operations except reflection in the plane of the molecule are concerned, as the 1s orbitals, so that we shall make up our symmetry orbitals from these in just the way we have already described. We are then left with two σ-type orbitals arising from the 2p electrons of each carbon. We naturally choose one of these with a nodal plane passing through the z axis, so that its wave function will change from - to + as the angle increases, and we may well call it a p_ϕ-type orbital; and we choose the other with a nodal plane tangent to a cylinder passing through the nucleus, so that its wave function will change from - to + as the radius increases, and we may call it a p_r-type orbital. The p_r-type has the same symmetry properties as the 1s, so that the discussion which we have already given applies to it. The p_ϕ-type is different, however, so that we must give it a special discussion.

With the atomic p_ϕ orbitals, there is no reason why we cannot use the method given in Eq. (3.1) of setting up symmetry orbitals, just as for the s orbitals. The only point which might be different from the s orbitals comes when we examine the behavior under reflection in the xz plane. Thus the wave functions for $m = 0$ and $m = 3$ are now antisymmetric in reflection in the xz plane, rather than symmetric as with the s orbitals. The reason is the nodal plane of the p_ϕ orbital. On reflection in the xz plane, the p_ϕ functions on atoms 3 and 6, which lie on the x axis, transform into the negatives of themselves. The function on atom 1 transforms into the negative of that on 5, and that on 2 transforms into the negative of that on 4. Hence we see the antisymmetry of the functions for $m = 0$ and 3 on reflection in the xz plane. By similar arguments, we can show that the function for $m = 0$ is antisymmetric on reflection in the yz plane, and that for $m = 3$ is symmetric. Using Eqs. (3.3) and (3.4), we can show that here, as with the s orbitals, the functions for $m = \pm 1, \pm 2$ can be written as sums of symmetric and antisymmetric functions on reflection in the xz plane.

We have concluded earlier that for the symmetry orbitals formed from s-like atomic orbitals, the states of lowest energy will be those with $m = 0$, with the energy increasing as m increases. Just the opposite, however, is the case with the p_ϕ-like orbitals. Thus for $m = 0$ we have a nodal plane in the form of a plane passing through the z axis, and through the nucleus of each atom; these nodal planes arise from the nodes present in the p_ϕ orbitals themselves. But in addition, we must have a nodal plane midway between these other planes, for the wave function changes from + to - as we go from one atom to the next, on account of the nature of the p_ϕ orbitals. For $m = 3$, on the contrary, where the p_ϕ orbitals have opposite signs on adjacent atoms, the orbitals of adjacent atoms add rather than subtracting at the point midway between atoms, and there are no extra nodal planes between atoms. Examination of the cases $m = \pm 1, \pm 2$ shows that these fall between the limiting cases $m = 0$ and 3. In other words, for p_ϕ-type orbitals, the symmetry orbital with fewest nodes, and with charge concentrated in the region between atoms, comes for maximum m, and we hence expect this to have the lowest energy; while the orbital with most nodes, located between atoms, which would be expected to have maximum energy, is that for $m = 0$.

We have now explored the types of symmetry orbitals which we can set up, and next we shall look at the extent to which the secular equation is factored on account of symmetry. In the first place, if we diagonalize the rotations, we can see at once that there can be no non-diagonal matrix components of energy between states of different m. Furthermore, on account of the diagonalization of the reflection in the plane of the molecule, there is no non-diagonal matrix component of energy between a σ and a π orbital. Thus in particular the symmetry orbitals formed from π electrons, corresponding to given m values, will be molecular orbitals, as far as our approximations extend. But we have five σ-type symmetry orbitals of each m value, corresponding to the hydrogen 1s orbital, the oxygen 1s, 2s, $2p_r$, and $2p_\phi$. Hence in general we may expect to have to solve a fifth degree secular equation between these, for each m value, unless there are additional symmetry features. For $m = 0$ and $m = 3$, there are such features: we have seen that in that case, the 1s, 2s, and $2p_r$ symmetry orbitals are symmetric on reflection in the xz plane, while the $2p_\phi$ symmetry orbitals are antisymmetric on reflection. Thus for $m = 0$ and $m = 3$, the secular equation factors, one factor representing the $2p_\phi$-type symmetry orbital, which itself forms a molecular orbital, and the other factor yielding a fourth degree secular equation between the symmetry orbitals arising from the hydrogen 1s, oxygen 1s, 2s, and $2p_r$. For $m = \pm 1, \pm 2$, however, this factorization does not occur; the $2p_\phi$ orbital gets mixed up with the others. In each case, of course, it may be legitimate, as in earlier cases, to assume that the oxygen 1s symmetry orbital forms approximately a molecular orbital by itself, without mixing up with the others. If this can be done, we are left with a cubic equation for $m = 0, 3$, and a fourth degree equation for the other values of m.

We may now make a guess as to the general nature of the one-electron energies. From the oxygen 1s orbitals, we shall have six molecular orbitals, all being very tightly bound, with small energy separation between the different m values. We shall expect $m = 0$ to lie lowest, $m = 3$ highest. Then from the σ orbitals of the carbons and hydrogens, we expect four groups of six orbitals, not very widely separated in energy. Let us first consider how these groups are likely to behave for $m = 0$, in which the orbital repeats periodically on each CH group. For $m = 0$, we remember that the three orbitals formed from the carbon 2s, the hydrogen 1s, and the carbon $2p_r$, do not combine with that formed from the carbon $2p\phi$. We consider first, then, the three combinations of the 2s, 1s, and $2p_r$. From our experience with the CO_2 case, we may expect that the lowest energy will be associated with a combination in which there are no nodes, except the nodes near the carbon nucleus coming from the inner node of the carbon 2s. There will be a maximum overlapping of charge between the carbon and hydrogen, and it is these orbitals which will be largely responsible for the binding between carbon and hydrogen. Such a combination will be made up of the carbon 2s and hydrogen 1s with the same sign, and a considerable contribution of the carbon $2p_r$ of such a sign as to reinforce the other wave functions in the region between carbon and hydrogen, and hence of such a sign as to tend to cancel the carbon 2s on the side away from the hydrogen, or toward the center of the benzene ring. In other words, the carbon 2s and $2p_r$ will combine in such a way as to give a maximum overlapping with the hydrogen 1s. This combination of orbitals on one CH group will now have its maximum intensity between the C and H, so that it will not be large between adjacent CH groups. Under these circumstances, we may expect that for the different m values, we have molecular orbitals arising from this combination of 1s, 2s, and $2p_r$, made up very much as indicated in Eq. (3.1), only now with this particular combination of hydrogen 1s and carbon 2s and $2p_r$ in place of the s_j appearing in that equation. Since the orbitals are not large in the region between carbons, we may expect that the energies of these orbitals will not depend greatly on m, though the energy will increase with m, since there is some slight tendency toward carbon-carbon bonding in these orbitals for the low m's, where the wave functions from adjacent CH groups add between the carbons, and a corresponding tendency against bonding for the high m's, where there are nodes between the carbons.

The orbitals we have been speaking of resemble the symmetric orbitals in the H_2 problem. At the opposite extreme are those resembling the antisymmetric orbitals in that problem. We may expect that the highest energy for $m = 0$ will correspond to a combination of hydrogen 1s, carbon 2s and $2p_r$, which has a node between the hydrogen and carbon. We should expect it to be made up from the same type of combination of carbon 2s and $2p_r$ as before, but combined with the hydrogen 1s with opposite sign. By analogy with the CO_2 problem which we have already discussed, we should expect that the coefficients of the functions would be so arranged that this wave function had three nodes, in addition to those near the carbon nucleus, since it corresponds to the highest energy of the three. For different m values, again, we should expect a set of orbitals with energy increasing with m, and probably again not varying greatly with m, since these functions do not correspond to large concentration of charge between the carbons.

Intermediate between these two types of orbitals, we must have a third one for m = 0 which does not correspond to any such large concentration of charge between the carbon and hydrogen as in the first case, and is more like a carbon 2s wave function alone, with just enough admixture of the carbon $2p_r$ and hydrogen 1s to give it one node. We should expect the charge distribution in this orbital to overlap those from neighboring carbons somewhat more than in the other two cases, so that the energy will increase rather more rapidly with m than for the other two types of orbitals.

We cannot consider this third type of orbital properly without also taking into account the orbitals made from the carbon 2p orbitals. We have already seen that for m = 0 and m = 3 the symmetry orbitals made from these 2p atomic orbitals according to the prescription of Eq. (3.1) will be molecular orbitals, without any mixture of other atomic orbitals, and that the lowest energy will come for m = 3, for which we have a large charge concentration between the carbons, while the highest energy will come for m = 0, for which we have nodes between the carbons. We conclude, then, that these orbitals are largely instrumental in the binding between carbons. We could attempt to plot the energy of these various types of orbitals, as a function of m, by drawing continuous curves, even though really the energy is defined only for the discrete values m = 0, ± 1, ± 2, 3. We shall see later that a simple symmetry orbital like that of Eq. (3.1) has a cosine-like curve giving energy as a function of m. If we draw such a curve for these orbitals coming from the atomic $2p_\phi$'s, our curve would have a maximum for m = 0, minimum for m = 3, while for the orbitals coming from the carbon 2s and $2p_r$, and hydrogen 1s, the minimum will come at m = 0, maximum at m = 3. It now seems very plausible that the energy curves, as drawn in this way, for the middle one of the three types of orbital formed from the carbon 2s and $2p_r$ and hydrogen 1s, will cross the curve formed from the carbon $2p\phi$, in approximately the center of the range, that is, between m = 1 and 2.

We have spoken as if there were continuous curves connecting these various energies, as functions of m. But we must remember that for m = ± 1, ± 2, the atomic orbitals $2p_\phi$ will combine with the 2s, $2p_r$, and hydrogen 1s; there is no symmetry property which states that they must be non-combining. If we really had solved a cubic secular equation for giving the best combinations of 2s, $2p_r$ and hydrogen 1s, for each m value, so as to give us an energy curve as a function of m for each of these three states, and had separately computed the energy of the symmetry orbital formed from the carbon $2p_\phi$'s for each m value, we should then find that there would be non-diagonal matrix components of energy between these states, for m = ± 1, ± 2, though not for m = 0, 3. If two of the curves crossed between m = 1 and 2, as we have postulated, when we neglect this interaction, our general knowledge of perturbation theory tells us that the interaction will push the two energy levels apart, and will give us new curves connecting the two lower branches of the interacting curves, and connecting the two upper branches. This presumably happens in our present case. Thus we may expect to have a lower set of orbitals, consisting for m = 0 of mostly a carbon 2s-like orbital, for m = 3 of a carbon $2p_\phi$-like orbital, with intermediate combinations between, but in each case having considerable charge concentration between the carbons; and an upper set, consisting for m = 0 of the carbon $2p_\phi$-like orbitals, for m = 3 of the combinations of hydrogen 1s, carbon 2s, and carbon $2p_r$, but in each case with a node between adjacent carbons. The orbitals of the lower set, in other words, tend to bond the carbons together, and of the upper set to make them repel.

We have now finished our catalog of the probable types of σ-orbitals for the benzene molecule. We have five types: the lowest type is almost exactly the carbon 1s, the next corresponds to charge concentration or bonding between each carbon and its adjacent hydrogen, the next to charge concentration or bonding between adjacent pairs of carbons, next to nodes or antibonding between adjacent carbons, and highest to nodes or antibonding between carbons and hydrogens. There is good chemical evidence that six out of the seven electrons in each CH group are actually located in σ orbitals. Thus we expect that the three lowest sets of six orbitals, in the catalog we have just given, are each occupied by two electrons, one of each spin, leaving the two higher sets of orbitals, corresponding to antibonding between carbon and carbon and between carbon and hydrogen, unoccupied. It is unfortunate that, in spite of all the work that has been done on benzene during twenty years, the straight-forward calculation of these σ-type molecular orbitals, and their one-electron energies, has not been made, and we are forced to rely on guesswork as to the probable nature of the energy values. Almost all the work on benzene has been concentrated on the π-electrons, which have interested the chemists on account of the way in which they led to an understanding of the relations between single and double bonds, but which are not inherently more important in understanding the problem that the σ-orbitals which have been so widely disregarded.

The problem of the π-electrons, which remains to be considered, is almost a trivial one compared to that of the σ-electrons, since we do not have any secular problem associated with them. The symmetry orbitals constructed from the atomic $2p_z$ orbitals according to Eq. (3.1) are the best representations which we have, consistent with our approximation scheme, for the corresponding molecular orbitals. The energy of the orbital for m = 0 will be lowest, that for m = 3 will be highest. The chemical evidence indicates that one electron per CH group is located in the π-orbitals, and hence we must conclude that the three lower orbitals, for m = 0, ± 1, are each filled with one electron of each spin, and the three upper ones, for m = ± 2, 3, are empty. This implies that the π energy levels for m = 0, ± 1 lie lower than the antibonding types of σ-electron orbitals which are unoccupied in the molecule, but that on the other hand the π levels for m = ± 2, 3, lie above any of the bonding types of σ-electrons which are occupied. This seems plausible, and if true it would lead to a complete description of the molecular orbitals of the benzene molecule, and their energy levels.

6. The Ammonia Molecule

In our summary of work by the molecular orbital method, we have mentioned that there has been a great deal of work on conjugated systems, chain-like planar structures composed of CH groups as in benzene, each group having six electrons in σ orbitals and one in a π-orbital. In many of these cases, there is a definite tendency to alternation which is not present in benzene: one bond definitely seems to be a single bond, the next one a double bond, and so on. Also there has been much work on substituted benzenes, in which a different atom is substituted for one or more of the hydrogens. Such problems are strikingly like those met in crystals; it must have been obvious that our treatment of the benzene molecule resembled that of a one-dimensional crystal with a periodicity of six atoms. The substituted benzenes, for instance, are very like crystals containing impurity atoms. Since we shall make a careful study of such problems when we come to the study of solids, it seems best to postpone these problems in molecular structure until we come to the similar problems in solids. We shall accordingly go ahead with a few other simple molecules at this point, to illustrate some features more typical of molecular than of solid-state structure. As a next illustration, we take the ammonia molecule, the first example we have taken up of a non-planar molecule.

The ammonia molecule, NH_3, consists of an equilateral triangle of hydrogen atoms, with a nitrogen atom on the line perpendicular to the plane of the hydrogens and passing through the center of the triangle, but some distance out of the plane of the hydrogens. In other words, the molecule forms a pyramid, with the nitrogen at the apex. Let us take the hydrogens to be in the xy plane, with one hydrogen on the x axis, and the origin at the center of the triangle, and let us take the nitrogen to be at a point on the positive z axis. Then the symmetry operations are very simple. They consist of rotations through 120° or any multiple of it about the z axis, and reflections in planes passing through the z axis, and making angles which are multiples of 60° with the xz plane. As in the case of benzene, we can see that these rotations do not commute with the reflections, but that we can generate all the symmetry operations from the rotations, and from reflection in the xz plane. Since the molecule is not planar, there is no symmetry operation connected with reflection in the xy plane.

If we diagonalize the rotations, then we see, by analogy with the case of benzene, that rotation through 120° must multiply the wave function by one of the cube roots of unity, or by $e^{2\pi i m/3}$, where $m = 0, \pm 1$. We see also that the two states with $m = \pm 1$ will be degenerate with each other, but not with the state $m = 0$. We must now construct symmetry orbitals out of the atomic orbitals of the nitrogen and hydrogens. First we consider how to do this with the hydrogen 1s orbitals. By analogy with Eq. (3.1), Section 5, we must merely make up the combinations $\sum(j)\, e^{2\pi i m j/3}\, s_j$, where s_j represents the hydrogen orbital on atom j, $j = 1$ corresponding to that at an angle 120° to the x axis, and so on. Thus for $m = 0$ the correct symmetry orbital is merely the sum of the hydrogen orbitals on all three atoms. From $m = \pm 1$, the symmetry orbitals are

$$s_3 - \frac{1}{2}(s_1 + s_2) \pm 0.866i(s_1 - s_2)\,. \qquad (3.5)$$

It is obvious that if we choose to diagonalize the reflection in the xz plane, rather than the rotation, then we should have chosen the two combinations $s_3 - 1/2(s_1 + s_2)$ and $0.866\ (s_1 - s_2)$ as our two symmetry orbitals, the first being symmetric, the second antisymmetric, in reflection in the xz plane. Here again, as with benzene, it is interesting to see that these two symmetry orbitals, though quite different in appearance, must be degenerate with each other.

Next we examine the way to make symmetry orbitals out of the nitrogen atomic orbitals. The method is obvious: we merely need set up the ordinary atomic orbitals, in which the component of angular momentum along the z axis is quantized. The nitrogen 1s, 2s, and the component of 2p corresponding to $m = 0$, are unchanged on rotation through any angle about the z axis, and hence in particular are unchanged on rotation through 120°, so that they have the same symmetry as our other orbitals corresponding to $m = 0$. Similarly, the nitrogen 2p corresponding to $m = \pm 1$ have the factor $e^{im\phi}$ in their wave functions, so that they are multiplied by the factor $e^{2\pi i/3}$ when we rotate through 120°, or $2\pi/3$. Thus they already have the proper form for symmetry orbitals. If we had chosen to diagonalize the reflection in the xz plane, we should merely have used the nitrogen $2p_x$, $2p_y$, $2p_z$ orbitals, of which the first and third are symmetric, the second antisymmetric, in this reflection.

We now have considered all the types of symmetry orbitals, and are ready to consider the nature of the secular problem leading to the molecular orbitals. For the orbitals with $m = 0$, we have combinations of the nitrogen 1s, 2s, and $2p_0$, and of the combination of the hydrogen orbitals corresponding to $m = 0$. Thus we shall have a fourth degree secular equation, which will reduce to a third degree equation if we assume that one solution is approximately the 1s orbital. Of the three remaining solutions, we may suppose that the lowest one corresponds to a bonding orbital between the nitrogen and the hydrogens. This would correspond to a combination of the nitrogen 2s and $2p_0$ of such a type that these would reinforce each other in the region between nitrogen and hydrogens, plus a contribution from the hydrogen $m = 0$ orbital, such that we should have a concentration of charge between the nitrogen and hydrogens. The second of these remaining solutions would presumably correspond to a concentration of charge largely on the nitrogen atom, with more charge on the side away from the hydrogens than toward them, and the third and highest would be a definitely antibonding combination with a node between the nitrogen and the hydrogens. For $m = 1$, we shall have two combinations of the nitrogen orbital $2p_1$ and the corresponding hydrogen symmetry orbital, one combination being a bonding one, with concentration of charge between nitrogen and hydrogens, and the other being antibonding, with a node between. The same thing will be true for $m = -1$.

In the ammonia molecule, we have ten electrons. Two will be in the 1s-like orbital, two in the bonding $m = 0$ orbital, two each in the bonding $m = \pm 1$ orbitals, and the remaining two in the $m = 0$ orbital concentrated largely on the nitrogen, in the direction away from the hydrogens. These two are lone-pair electrons, in the sense of Lennard-Jones, as we saw that there were four lone-pair electrons in the water molecule. They are the electrons that tend to attract an additional proton, forming the ammonium ion $(NH_4)^+$, which has the same tetrahedral structure as methane, which we shall discuss next. Finally, the antibonding orbitals are empty.

An interesting question connected with the ammonia molecule is why it is not planar. To answer this question properly, we should have to calculate the energy as a function of the distance of the nitrogen from the plane of the hydrogens, allowing the triangle of hydrogens to adjust itself, for each position of the nitrogen, to a size correct to give minimum energy. Then we should have to find the total electronic energy of the molecule as a function of nitrogen position, and see where the minimum came. The experimental situation is well known: there are two rather shallow minima of energy, one with the nitrogen on each side of the plane of the hydrogens, with a maximum of energy when the nitrogen is in the plane. On the other hand, this energy maximum in the plane is not very high above the minima, so that the tendency away from planar configuration is not very strong. Though we cannot predict this situation from our qualitative discussion of molecular orbitals, at least we can easily see the features which will go into the calculation.

In the first place, there is naturally a repulsion between the hydrogen atoms and the inner K shell of the nitrogen, which will tend to keep the hydrogens at some distance from the nitrogen. This repulsion would come in, in our picture, if the nitrogen-hydrogen distance were small enough so that the nitrogen 1s and hydrogen 1s wave functions were appreciably mixed in any of the molecular orbitals. It would tend to hinder the nitrogen from squeezing through the center of the hydrogen triangle. More important, however, would be the effect on the nitrogen-hydrogen bonds of a displacement of the nitrogen. With the non-planar arrangement, we have seen that the bonding orbitals of $m = 0$ type will be a combination of nitrogen 2s, $2p_0$, and the hydrogen orbitals. If we had a planar molecule, the $2p_0$ would become a π electron, forbidden by symmetry to combine with the 2s and the hydrogen orbitals, and this would presumably decrease the strength of the nitrogen-hydrogen binding. This is probably the main effect tending to favor the non-planar configuration. It is partly counterbalanced, however, by an effect met with the $m = \pm 1$ orbitals. These, as we have seen, are made out of hydrogen orbitals, and nitrogen 2p orbitals with $m = \pm 1$. These nitrogen orbitals have maximum values in the plane perpendicular to the z axis, and hence if the molecule had a planar configuration, they would have a maximum overlap with the hydrogen orbitals, and a maximum binding effect. This will be somewhat weakened in the non-planar configuration, and we must assume that this weakening is not enough to counteract the strengthening of the binding coming from the $m = 0$ orbitals. From this rather complicated interplay, we see that it would be dangerous to go too far in making qualitative predictions, without quantitative calculations of the actual energy levels as a function of nuclear positions. Such quantitative calculations do not seem to have been made.

7. The Methane Molecule

The methane molecule, CH_4, has a tetrahedral structure, with the carbon in the

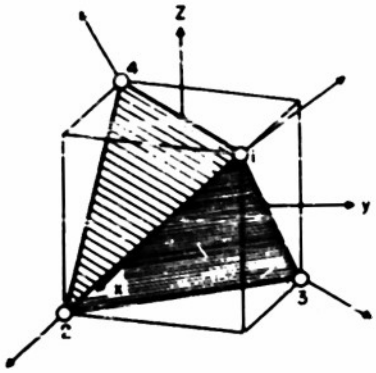

Fig. 5

center. This molecule is most conveniently shown as in the diagram of Fig. 5, where the carbon is at the origin, and the hydrogens occupy four of the eight corners of a cube. Thus if the sides of the cube are two units in length, the carbon which we have denoted (1) has the coordinates (1, 1, 1); that which we have denoted (2) has coordinates (1, - 1, - 1); (3) has (- 1, 1, - 1); and (4) has (- 1, - 1, 1). We see that there are many symmetry operations which transform the molecule into itself. Thus in the first place, we can rotate through 180° about the x, y, or z axes. These two-fold axes of rotation are those drawn from the carbon out to the centers of the lines joining the pairs of hydrogens. Associated with these two-fold rotations there are of course certain reflections. Thus we can reflect in a plane passing through the x axis and through the two atoms (1) and (2); or in a plane passing through the x axis and perpendicular to this. From what we have already seen, successive reflection in these two planes are equivalent to the rotation. In regard to our three two-fold axes of rotation, the first thing to notice is that these three rotations commute with each other, so that they can all be simultaneously diagonalized, and this is the method of diagonalization which we shall prefer. Thus rotation through 180° about the x axis transforms the coordinates (x, y, z) into (x, - y, - z). Rotation through 180° about the y axis transforms (x, y, z) into (- x, y, - z). Successive application of these two rotations, in either order, transforms (x, y, z) into (- x, - y, z), so that they commute; furthermore, it is clear that the successive application of these rotations is equivalent to rotation of 180° about the z axis.

In addition to these three two-fold axes of rotation, there are four three-fold axes, indicated by 1, 2, 3, 4 in Fig. 5. By a three-fold axis, we mean that rotation through $2\pi/3$, or 120°, brings the molecule back into coincidence with itself. Thus these axes point out from the carbon to the four hydrogens, and rotation through 120° about axis 1 shifts hydrogen 2 to position 3, 3 to position 4, and 4 to position 2. These three-fold rotations do not commute with each other, or with the two-fold rotations. This statement is a special case of the general theorem that two rotations around different axes do not commute with each other provided the angle between axes is different from 90°; and even if the angle is 90°, they commute only if the rotations are through angles of 180°. Let us examine the reason for this general theorem. In the first place, we can easily convince ourselves that it can only be in very special cases that rotations about different axes should commute. We can, for instance, write one rotation as a linear transformation of the coordinates x, y, z to new coordinates x', y', z', the coefficients of the transformation satisfying the orthogonality conditions; similarly the second rotation is written as another linear transformation from x', y', z' to x'', y'', z''. Then we can express the coefficients of the combined transformation from x, y, z to x'', y'', z'' in terms of the separate coefficients, and we find that there is nothing inherent in the problem which leads to the result being the same independent of the order of the rotations.

For rotations about axes at right angles to each other, however, we have a special case, which we may examine separately. Thus let us choose the two axes as the x and y axes. Let the first rotation be around the x axis, though an angle θ. Then we have $x' = x$, $y' = y \cos\theta + z \sin\theta$, $z' = -y \sin\theta + z \cos\theta$. Similarly let the second rotation be around the y axis, by an angle ϕ. Then $x'' = x' \cos\phi - z' \sin\phi$, $y'' = y'$, $z'' = x' \sin\phi + z' \cos\phi$. When we combine these expressions, we have

$$\begin{aligned} x'' &= x \cos\phi + y \sin\theta \sin\phi - z \cos\theta \sin\phi \\ y'' &= y \cos\theta + z \sin\theta \qquad\qquad (3.6) \\ z'' &= x \sin\phi - y \sin\theta \cos\phi + z \cos\theta \cos\phi \end{aligned}$$

Now we may perform the operations in the opposite order. Thus we have $x' = x \cos\phi - z \sin\phi$, $y' = y$, $z' = x \sin\phi + z \cos\phi$, and $x'' = x'$, $y'' = y' \cos\theta + z' \sin\theta$, $z'' = -y' \sin\theta + z' \cos\theta$. Combining these expressions, we have

$$\begin{aligned} x'' &= x \cos\phi - z \sin\phi \\ y'' &= x \sin\theta \sin\phi + y \cos\theta + z \sin\theta \cos\phi \qquad\qquad (3.7) \\ z'' &= x \cos\theta \sin\phi - y \sin\theta + z \cos\theta \cos\phi . \end{aligned}$$

If the two rotations are to commute with each other, this means that Eq. (3.7) must be identical with (3.6). For this to happen, excluding the trivial case of $\theta = 0$, $\phi = 0$, we must have $\sin\theta = 0$, $\sin\phi = 0$, which means $\theta = \pi$, $\phi = \pi$ (since the possibilities 0 are excluded). In other words we have proved our result that two rotations about axes at right angles to each other commute only if each rotation is through 180°. In this case, our final expressions are $x'' = -x$, $y'' = -y$, $z'' = z$, equivalent to a rotation of 180° about the z axis.

There is an interesting application of this fact, that two rotations about axes at right angles to each other do not commute if the angles of rotation are anything but 180°. This relates to the non-commuting nature of the angular momentum operators corresponding to x, y, and z components of angular momentum, discussed for instance in QTM, pp. 479-485. We can show by elementary methods that the operator associated with the z component of angular momentum is $(h/2\pi i)(\partial/\partial\phi)$, where ϕ is the angle of rotation about the z axis, in polar coordinates. That is, if the wave function is $u(r, \theta, \phi)$, if the operator is M_z, and if we write the derivative as the limit of the difference, we have

$$M_z u = \frac{h}{2\pi i} \lim_{\delta\phi = 0} \frac{u(r, \theta, \phi + \delta\phi) - u(r, \theta, \phi)}{\delta\phi} .$$

If we assume that this is approximately correct for a small but finite $\delta\phi$, we may then approximately write

$$\left(1 + \frac{2\pi i}{h}\,\delta\phi M_z\right) u(r, \theta, \phi) = u(r, \theta, \phi + \delta\phi) .$$

In other words, the operator on the left, a linear function of M_z, is one which transforms the function $u(r, \theta, \phi)$ by rotating through an angle $\delta\phi$ around the z axis. Similarly an equivalent operator made from M_x transforms by rotation around the x axis, and similarly for the y axis. Since we have just found that rotations around the x, y, and z axes do not commute unless they are through angles of 180°, we see that the fact that M_x, M_y, and M_z do not commute is directly tied up with our present results.

Returning to the problem of methane, we see that our commuting rotations around two perpendicular axes are of the form which we have already found for the three two-fold axes in our problem, and that these represent the only type of commuting rotations around different rotation axes which can exist. Thus we prove our statement that rotations around the four three-fold axes do not commute with each other, or with the two-fold rotations. Under the circumstances, then, the best thing we can do is simultaneously to diagonalize the rotations around the two-fold axes, leaving the three-fold rotations with non-diagonal matrices. We must obviously have degeneracy in the problem, and we shall see just what sort when we set up our symmetry orbitals.

We wish to make up symmetry orbitals out of the four hydrogen 1s orbitals, and out of the carbon atomic functions. It is at once obvious how to do this with the carbon functions. The carbon 1s and 2s functions are already proper symmetry orbitals: they are unchanged under any one of the rotations. In addition to these, we can choose the carbon $2p_x$, $2p_y$, and $2p_z$ orbitals. Under the rotation of 180° around the x axis, $2p_x$ is symmetric and $2p_y$ and $2p_z$ antisymmetric, so that each of these is diagonalized for these rotations. On the other hand, if we had preferred to diagonalize one of the three-fold rotations, say around the axis pointing to atom (1), we should have chosen the carbon 2p wave functions having their components of angular momentum around this axis quantized. The problem then would be set up by analogy with the ammonia problem, showing the same three-fold rotational behavior, with the molecular orbitals characterized by quantum numbers m, which could equal 0, ± 1, with the two states ± 1 degenerate with each other.

We can now very easily set up the four combinations of the four hydrogen 1s functions which are symmetry orbitals for the two-fold rotations. If we symbolize the hydrogen functions by s_1, s_2, s_3, s_4, the hydrogens being numbered as in Fig. 5, then we have one combination $s_1 + s_2 + s_3 + s_4$ which is unchanged under any of the rotations; this particular function, then, acts like the carbon s states as far as our symmetry operations are concerned. This particular function is obviously unchanged as well under a rotation around one of the three-fold axes. In addition to this function, we have three combinations which have the symmetry of the carbon $2p_x$, $2p_y$, and $2p_z$ functions respectively. Thus the combination $s_1 + s_2 - s_3 - s_4$ is unchanged on rotation through 180° about the x axis, but changes sign on rotation about the y or x axes, just as $2p_x$ does. Similarly the combination $s_1 - s_2 + s_3 - s_4$

acts like $2p_y$, and $s_1 - s_2 - s_3 + s_4$ acts like $2p_z$. These four combinations form the symmetry orbitals of the problem.

Before we use these symmetry orbitals, let us see how they behave under the three-fold rotations, to check the fact that each one transforms into a combination of the others. Let us consider the rotation about the axis 1, in which x is rotated into y, y into z, z into x. That is, if we start with a molecular orbital u(x, y, z), we transform to u(y, z, x). Obviously one of the s atomic orbitals of the carbon will transform into itself. The $2p_x$ orbital, however, whose wave functions is x f(r), where r is the radius, will transform into y f(r), which equals $2p_y$, and similarly $2p_y$ will transform into $2p_z$, $2p_z$ into $2p_x$. To see how the hydrogen orbitals transform, let us first examine the transformation properties of the functions s_1, s_2, s_3, s_4. These are functions of the distance from the respective hydrogen nuclei. The nuclei have coordinates given respectively by (a, a, a), (a, -a, -a), (-a, a, -a), (-a, -a, a), if a is the half-side of the cube in Fig. 5. Thus $s_1(x, y, z)$ is a function $F\left\{(x - a)^2 + (y - a)^2 + (z - a)^2\right\}^{1/2}$. When we make the transformation $(x, y, z) \rightarrow (y, z, x)$, this obviously transforms into itself. Similarly $s_2(x, y, z) = F\left\{(x - a)^2 + (y + a)^2 + (z + a)^2\right\}^{1/2}$, which transforms into $F\left\{(x + a)^2 + (y - a)^2 + (z + a)^2\right\}^{1/2}$, which equals $s_3(x, y, z)$, and s_3 transforms into s_4, s_4 into s_2. Thus we see that under this rotation, the function $s_1 + s_2 + s_3 + s_4$ transforms into itself, the function $s_1 + s_2 - s_3 - s_4$ transforms into $s_1 - s_2 + s_3 - s_4$, or the p_x-like combination of hydrogen orbitals transforms into the p_y-like, and so on with the others. In other words, we see how our three-fold rotation axis ties in with the three-fold degeneracy of the symmetry orbitals, and we see that the combinations of hydrogen orbitals which we have made transform as they should, and as the carbon atomic orbitals do, under the three-fold as well as the two-fold rotations.

Let us now see how these symmetry orbitals combine into molecular orbitals. We have three orbitals of s-like symmetry: the carbon 1s, 2s, and the s-like combination of the four hydrogen orbitals. Of the three combinations of these, one will be very nearly the carbon 1s, a second will be a combination of the carbon 2s and the hydrogen orbitals having a maximum between carbon and hydrogens, and hence of bonding character, and the one of highest energy will be an antibonding combination of carbon 2s and hydrogen orbitals, with a nodal surface (roughly a sphere) between the carbon and the hydrogens. There are two orbitals of p_x-like symmetry, the carbon $2p_x$, and the combination of hydrogen orbitals of this same symmetry. Here we shall have a bonding combination of carbon and hydrogen orbitals, with a maximum between the atoms, and an antibonding orbital of higher energy, with a nodal surface between carbon and hydrogens. The methane molecule now has ten electrons, just like the neon atom, and these are just enough to fill the 1s-like orbital, the bonding s-like combination of carbon and hydrogen, and the bonding p_x-like, p_y-like, and p_z-like combinations of carbon and hydrogen, leaving the antibonding orbitals empty. As we look at these wave functions, we see that the situation is strikingly like that found in the neon atom. The antibonding combinations of carbon and hydrogen orbitals, having an extra node roughly in the form of a sphere, have very much the character of the 3s, $3p_x$, $3p_y$, and $3p_z$ orbitals of an atom, and these are the orbitals which are unoccupied in the ground state of the methane molecule.

8. General Determination of Molecular Orbitals

We have now examined enough types of molecules, and the symmetry relations of their molecular orbitals, so that the reader will be familiar with the general principles determining these orbitals. There are of course many other configurations which molecules can have, but the number of symmetry types is not unlimited, and we have taken up many, though not all, of the important ones. We shall now go on to the other part of the problem, the setting up of the secular equation for determining the molecular orbitals. We shall consider the case which we have been assuming in the preceding sections: that in which we build up an approximate molecular orbital as a linear combination of atomic orbitals.

We start with a set of atomic orbitals, which we may call χ_i. These functions, just like the ones we have been speaking of, are atomic orbitals on various atoms, functions of the distance of the nucleus multiplied by a spherical harmonic of the angle. From these atomic orbitals we construct symmetry orbitals, which we may call ψ_i, by the methods we have described. These symmetry orbitals are linear combinations of the atomic orbitals; we may write $\psi_i = \sum(j)\, C_{ij}\, \chi_j$. We have not so far said anything about the orthogonality of these symmetry orbitals. The atomic orbitals are not orthogonal to each other; we may define $\int \chi_i{}^* \chi_j \, dv = S_{ij}$, where $S_{ii} = 1$, the atomic orbitals being normalized, but where the non-diagonal components S_{ij}, $i \neq j$, represent overlap integrals which do not vanish. Two symmetry orbitals of different symmetry type are automatically orthogonal to each other, but two of the same type do not have to be. It is, however, much more convenient to deal only with orthogonal orbitals, and for this reason it is generally convenient to set up the symmetry orbitals so that they are orthogonal to each other. This can be done in an infinite number of ways, since if we have n symmetry orbitals of a given type, any n orthogonal linear combinations of them will serve equally well as symmetry orbitals, and the final answer will not depend on how we orthogonalize them. One standard procedure for orthogonalizing is to number the symmetry orbitals from 1 to n (say starting with the most tightly bound), then use 1 as one of the orthogonalized orbitals, use a linear combination of 1 and 2 with coefficients chosen so as to make it orthogonal to 1 as a second, a linear combination of 1, 2, and 3 with coefficients chosen to make it orthogonal to the first two as the third, and so on. We shall assume from now on that this orthogonalization has been carried out, so that the functions ψ_i are orthogonal and normalized.

In the self-consistent field method, as we have outlined it, we have a one-electron potential V, and a one-electron Hamiltonian H. We wish then to find the matrix components of this Hamiltonian with respect to the symmetry orbitals ψ_i; these matrix components lead at once to the secular equation which determines the molecular orbitals and one-electron energies. On account of the fundamental properties of the symmetry orbitals, there will be no non-diagonal matrix components between orbitals of different symmetry. Between two orbitals ψ_i and ψ_j of the same symmetry, the matrix component will be

$$\int \psi_i^* H \psi_j \, dv = \sum(km) C_{ik}^* C_{jm} \int \chi_k^* H \chi_m \, dv . \tag{3.8}$$

Since we know the C's, this at once allows us to compute the desired matrix components from the components $\int \chi_k^* H \chi_m \, dv$ of the one-electron energy with respect to the atomic orbitals. Let us next consider how to find these components.

The operator H equals the kinetic energy operator, plus the potential energy V of the self-consistent field. We assume that the χ's are atomic orbitals, which means that they are solutions of a self-consistent field problem of some sort for an atom. That is, if V_o is the potential energy of this central field, and if H_o is an energy operator consisting of the kinetic energy plus V_o, we have $H_o \chi_m = \epsilon_m \chi_m$, where ϵ_m is the one-electron energy. If the χ's are not actual solutions of an ordinary self-consistent field problem, we still can set up a V_o and an H_o such that this equation will be satisfied. Then we clearly have $H\chi_m = (H_o + V - V_o)\chi_m = (\epsilon_m + V - V_o)\chi_m$. From this we then see that

$$\int \chi_k^* H \chi_m \, dv = \epsilon_m S_{km} + \int \chi_k^* (V - V_o) \chi_m \, dv . \tag{3.9}$$

Integral of the type appearing in Eq. (3.9), then, are the ones which must be determined to get the matrix components of H.

The potential V, by its nature, behaves very much like an atomic potential around each atom of the molecule. It is approximately like a sum of spherically symmetrical potentials, one located at each atom, and near the atom on which χ_m is located, it will be approximately equal to V_o, the atomic potential on that atom. Thus $V - V_o$ resembles a sum of spherically symmetrical potentials, located on all the atoms except that where χ_m is located, that one being approximately cancelled. Thus to an approximation the integral of Eq. (3.9) is a sum of terms, each being a product of two atomic orbitals on two different atoms, and of a spherically symmetrical potential located on a third atom. Such an integral is called a three-center integral. It is a hard thing to compute, but analytical methods are available for finding it. These methods amount to expanding the atomic function, say χ_m, located at one atom, in terms of functions of r and spherical harmonics about another center, in this case the center where the spherically symmetrical potential is located. Once the atomic functions are expanded about this center, the integral becomes simple.

Even without this complicated mathematics, we can see directly the general nature of the expression (3.9). The integral vanishes unless there are some parts of coordinate space where χ_k, χ_m, and one of the spherical potentials out of which V is constructed, are simultaneously different from zero. The largest terms will come when χ_k and χ_m are on adjacent atoms, and when we use that term of $V - V_o$ representing the potential on the atom where χ_k

is located. It is then clear that the more the two wave functions χ_k and χ_m overlap, the greater will be the integral. It is this general type of argument which shows us that bonding orbitals are those with large overlapping of adjacent wave functions.

These general remarks will become plainer if we work through a specific case, and a very interesting one is that of finding the diagonal matrix components of energy for the π orbitals of benzene. This is one of the first cases where molecular orbital energies were really computed, in the work of Hückel which has been quoted earlier. The symmetry orbitals, as we see from Eq. (3.1), Section 5, are of the form $\sum(j)\, e^{imj\pi/3}\, s_j$, where the s_j's are atomic orbitals on the various atoms. These wave functions, in the first place, are not normalized. Let us then carry out this normalization. To do so, we multiply the wave function by its conjugate, and integrate over all values of the coordinates. The result is evidently

$$\sum(j, k)\, e^{im(k-j)\pi/3}\, S_{jk}, \tag{3.10}$$

where as before S_{jk} is the overlap integral, $\int s_j^* s_k\, dv$. Now we notice that on account of the rotational symmetry of the molecule, this overlap integral S_{jk} depends only on the difference $k - j$ between the atoms, as measured around the ring. Thus the summation in (3.10) may be converted into a double sum, first over the difference $k - j$, which is to go over all values from 1 to 6, and then over j itself. Furthermore, the quantity being summed depends only on $k - j$, so that this last summation merely multiplies the result of the earlier summation by 6. A further thing which we may notice is that $S_{jk} = S_{kj}$, if we are dealing with real atomic orbitals, since in such case $S_{jk} = \int s_j s_k\, dv$, obviously independent of the order of summation.

We may now put these pieces of information together, and we find for the summation in (3.10)

$$6(1 + 2\cos m\pi/3\, S_{01} + 2\cos 2m\pi/3\, S_{02} + \cos m\pi\, S_{03}) \tag{3.11}$$

Here S_{00}, which is not written down, is unity, since the s's are assumed to be normalized, and S_{01}, S_{02}, S_{03} are respectively the overlap integrals between an atomic orbital and its nearest neighbor, next nearest neighbor, and finally the orbital diametrically opposite it. Thus we find that the normalized symmetry orbital is

$$\frac{\sum(j)\, e^{imj\pi/3}\, s_j}{6^{1/2}\left\{1 + 2\cos m\pi/3\, S_{01} + \ldots + \cos m\pi\, S_{03}\right\}^{1/2}} \tag{3.12}$$

Next we wish to find the diagonal matrix component of energy for this orbital; that is, the one-electron energy. Since in the benzene problem there are no other orbitals having the same symmetry, there is no secular problem to be solved to find the one-electron energy, and no non-diagonal matrix components of energy to be computed. To find the diagonal matrix component, we must let H operate on the function (3.12), multiply by the conjugate of

(3.12), and integrate over the coordinates. As in (3.8), this immediately breaks down into a summation of matrix components $\int s_k H s_m \, dv$ of the Hamiltonian between atomic orbitals, and each of these components can be written out by Eq. (3.9). The double sum arising from (3.8) can be handled just like that which we have already met in Eq. (3.10), in connection with the normalization problem. When we do this, we find at once

$$E_m = \frac{H_{00} + 2\cos m\pi/3 \, H_{01} + 2\cos 2m\pi/3 \, H_{02} + \cos m\pi \, H_{03}}{1 + 2\cos m\pi/3 \, S_{01} + 2\cos 2m\pi/3 \, S_{02} + \cos m\pi \, S_{03}} \tag{3.13}$$

where E_m is the appropriate one-electron energy. Here we have written H_{km} for the matrix component $\int s_k H s_m \, dv$ between the kth and m^{th} atomic orbitals, and as with the overlap integrals, this will depend only on the distance between the atoms k and m. If we now use Eq. (3.8), and let $U_{km} = \int s_k (V - V_o) \, s_m \, dv$, we can rewrite (3.13) in the form

$$E_m = \epsilon_0 + \frac{U_{00} + 2\cos m\pi/3 \, U_{01} + 2\cos 2m\pi/3 \, U_{02} + \cos m\pi \, U_{03}}{1 + 2\cos m\pi/3 \, S_{01} + 2\cos 2m\pi/3 \, S_{02} + \cos m\pi \, S_{03}} \tag{3.14}$$

where ϵ_0 is the one-electron energy of the atomic orbital.

Let us now consider the dependence on m which Eq. (3.14) indicates. In the first place, considering E_m as a continuous function of the variable m, we see that it is periodic with m, with period 6. Thus, when we were discussing benzene, and considering the energy as a function of M from m = - 3 to + 3, we could have considered the function to repeat periodically outside this range. This is just like the behavior of the energy as a function of momentum in the periodic potential problem in a crystal, where the energy is a periodic function of position in the reciprocal space. Furthermore, the leading term in Eq. (3.14), aside of course from the atomic energy ϵ_0, is the term 2 cos $m\pi/3 \, U_{01}$ in the numerator. The reason for this is the following. First, U_{00} is very small. This is the integral of the square of an atomic orbital, times the function $(V - V_o)$, which is small within the atom in question, since V and V_o nearly cancel there, and which is large only in other atoms, where the atomic orbitals are small. Secondly, U_{02} and U_{03}, coming from more distant neighbors than U_{01}, will be smaller since they involve orbitals which overlap much less. As far as the denominator is concerned, if the orbitals are far enough apart so that they do not overlap very greatly, the S's will not be very large, and the first term, unity, will be the leading term, though as we see from the example of the hydrogen molecule as discussed in Chapter 2, the S's can sometimes be large enough so that they are very important. In any case, the general trend of the variation of E_m with m is likely to be set more or less by the term 2 cos $m\pi/3 \, U_{01}$.

Now the quantity U_{01}, for orbitals like the $2p\pi$'s of benzene, will be negative. We can see that from Eq. (3.8). In the first place, V is negative, and V_o does not entirely cancel it, so that $V - V_o$ is negative. Furthermore, the orbitals s_0 and s_1 are of the same sign where they overlap. Thus if they are 2pπ's, they are positive everywhere on the positive side of the plane of the molecule, and negative everywhere on the negative side, so that in either case their product is positive. Hence the integral U_{01} must be negative, as we have stated. Therefore the energy, as given in Eq. (3.14), will have a minimum at $m = 0$, a maximum at $m = 3$, as we have indicated in our qualitative discussion of the energy levels of benzene. On the other hand, if we consider the type of atomic orbital which we denoted as 2pϕ in the discussion of benzene, we see that two such orbitals on adjacent atoms will have opposite sign in the region where they overlap most strongly. Thus the integrand involved in finding U_{01} in such a case will be positive, and U_{01} itself will be positive, requiring for such an orbital in a maximum of one-electron energy for $m = 0$, a minimum for $m = 3$, as we indicated. Of course, it is clear that in an actual case the various quantities U_{00}, U_{01}, U_{02}, U_{03}, S_{01}, S_{02}, S_{03} in (3.14) may all be of significant magnitude, and they must all be considered. When they are fairly large, the function of m given in (3.14) may be quite complicated, quite different from the simple term $2 \cos m\pi/3\ U_{01}$ which we have regarded as its leading term. In some calculations on such problems, these terms have been all taken into account, but there has been an unfortunate tendency here, as in so many problems of molecular and solid-state theory, to make unwarranted assumptions that certain terms are small. Thus the overlap integrals in the denominator of (3.14) have often been disregarded. We can see how unjustified this can be by recalling that the overlap integral between two hydrogen orbitals at the equilibrium internuclear distance in the molecule (about 1.5 atomic units) is about 0.72, as we see from Table II, page 52.

The example which we have given, from the benzene problem, will illustrate the way in which diagonal matrix components of energy may be obtained for the symmetry orbitals; the method for non-diagonal components is very similar. We thus understand the general method used in finding molecular orbitals by the LCAO method. We must realize that in the discussions of the present chapter, we have described how to make linear combinations of a very few symmetry orbitals, which may represent approximations to the real molecular orbitals. It is of course obvious that if we had a complete orthogonal set of symmetry orbitals to start with, we could determine the molecular orbitals with perfect accuracy, provided we solved the secular equation between all these symmetry orbitals. This is naturally an impossible program to carry out, and we may only hope that by using the very small number of symmetry orbitals we have considered, the approximation will not be too bad. It will presumably be found that as the subject progresses, workers will find it advisable to use a larger set of symmetry orbitals, and solve larger secular equations, in order to get better molecular orbitals. This more extended set of symmetry orbitals may not necessarily be best written as linear combinations of atomic orbitals. Study of the corresponding problem in solids shows that the LCAO method is very good for making symmetry orbitals corresponding to the actually occupied energy levels, but that for higher orbitals it can be very poor. We shall merely mention this restriction as a warning, and shall expand on it later when we come to consider crystals.

The setting up of the secular equation between the symmetry orbitals is of course only part of the self-consistent field problem. The other part is the determination of the potential V from the self-consistent wave function. If this wave function is a single determinant made up of molecular orbitals, as we are assuming in this chapter, then we have the problem discussed in Chapter 1, of finding a self-consistent field. Thus we may use Eq. (1.21) of that chapter to get a Schrödinger equation, and the expression for the effective charge density of other electrons will be as given in Eq. (1.19) of that chapter. The potential, as computed from these equations, is difficult but not at all impossible to find. It involves integrals which amount to finding the potential, at an arbitrary point, of a charge distribution given by the product of atomic orbitals, on the same or different atoms. Methods of finding such potentials are well known. The molecular orbitals which appear in (1.19) are of course the linear combinations of symmetry orbitals, which in turn are linear combinations of atomic orbitals, which we have already found, but the expression (1.19) can then be broken down into a sum of terms each of which is a potential coming from two atomic orbitals, of the type just mentioned. Thus there is nothing in principle impossible about calculating this self-consistent field, though in practice it may be tedious.

When the calculation has been carried out, it will probably be expressed in an unwieldy form for analytic calculation. As a general rule, it will be desirable to attempt to fit it approximately with a sum of spherically symmetrical potentials located around the various atoms, in the manner sketched above. In general it will not be possible to do this exactly, but it should not be impossible to do it fairly accurately, and the difference could be treated as a small correction term. A general self-consistent field calculation following the lines just sketched has not been made for any molecule, but the writer believes it to be practicable, and probably as good as any other method.

The few calculations which have been made fairly quantitatively by the molecular orbital method, however, have used a closer analogue to the Hartree-Fock equation. This has involved using essentially Eq. (1.16) of Chapter 1, rather than (1.21), obtaining therefore a different Schrödinger equation for each molecular orbital. The one-electron orbitals appearing in (1.16) are taken to be the linear combinations of symmetry orbitals which we have already described as molecular orbitals, and (1.16) furnishes us with a one-electron Hamiltonian operator, whose matrix components between the various molecular orbitals can be found essentially by methods already described. It is this method which has been used by Roothaan, Mulligan, Mulliken, and others, in papers to which we have already referred, or which appear in the bibliography. This Hartree-Fock method is certainly better than the method of Eq. (1.21) for a single determinantal wave function, in the sense that it determines the molecular orbitals in the most accurate way possible. On the other hand, for the reasons described in Section 8, Chapter 1, the writer believes that the method discussed in that section has some advantages over the Hartree-Fock method which make it desirable for the general determination of molecular orbitals. The difference between the two methods, however, is certainly small, and considering the many approximations always made in such calculations, it is probably immaterial which method is used.

CHAPTER 4

CONFIGURATION INTERACTION IN MOLECULES

The method of molecular orbitals, as we have described it in the preceding chapter, forms a first step toward a program which in theory could result in exact wave functions for molecules. That is, we could start with a potential V, as derived from a self-consistent field method, and a one-electron Hamiltonian H associated with it. We could, in principle, find an infinite set of solutions of the one-electron problem resulting from this Hamiltonian, forming a complete orthogonal set of one-electron functions. We could pick out sets of n such one-electron functions of coordinates and spin, where n is the number of electrons, in all possible ways, forming a determinantal function from each such choice. Then we have a complete orthogonal set of determinantal functions, such that a suitable linear combination of them will represent any antisymmetric function of electronic coordinates and spins with any desired degree of accuracy. To get the expansion of the correct wave function as a sum of such determinantal functions, we find the matrix components of the many-electron Hamiltonian of the problem between these determinantal functions, and solve the resulting secular equation. If we refer to each choice of n one-electron functions, and each determinantal function, as a configuration, this problem becomes the general one of configuration interaction, and we see that in principle a complete treatment of configuration interaction yields a complete solution of the problem.

Of course, this ideal procedure is far beyond our capabilities to carry out. We may, however, build quite practicably on the methods which we have been describing in the preceding chapter, and get something which can really be handled. Thus in the preceding chapter we showed how we could set up symmetry orbitals, as linear combinations of atomic orbitals. Then we showed how to make linear combinations of these symmetry orbitals, and to solve the secular equation for the one-electron problem, in such a way as to get those linear combinations of the symmetry orbitals which represented the molecular orbitals as well as possible. In this way we got in each case a very restricted number of approximate molecular orbitals, and found how to get their one-electron energies. We then made just one determinantal combination of these molecular orbitals, using those of lowest one-electron energies, and considered that this formed an approximation to the lowest wave function of the molecule. We could, however, have formed a limited number of other determinantal functions from these molecular orbitals, by choosing different configurations, and could have considered the configuration interaction between these. As we shall show in this chapter, in some cases the resulting number of configurations is not too great to handle, and such a treatment of configuration interaction is practicable and informing.

A very important feature of such treatments of configuration interaction is the way in which they embody in themselves various other methods of approximation. Thus in the problem of the hydrogen molecule, which we took up in detail in Chapter 2, we found that if we used just two molecular orbitals, the symmetric and antisymmetric combination of the atomic orbitals on the two atoms, and set up all the combinations of determinantal functions resulting from them, we achieved the same results as if we had started with the Heitler-London method, included ionic as well as non-ionic states, and carried out a secular problem of interaction between these wave functions. Our method of handling configuration interaction, as we shall describe it in this chapter, is the direct extension of this method to more complicated molecules, and in the same way it achieves all that the Heitler-London method, when supplemented by ionic states, can do. It seems like the straightforward way of extending the Heitler-London method to more complicated molecules than hydrogen. We remember that, in our discussion of the hydrogen molecule, we found that the single molecular orbital state did not go to the correct energy at infinite internuclear distance, though the Heitler-London method did, and the solutions found by configuration interaction, starting with the molecular orbital functions, behaved properly at infinite distance. In the same way here we shall find that the shortcomings of the molecular orbital method at infinite internuclear distance are removed by considering configuration interaction.

In our chapter on the hydrogen molecule, we followed through with three independent methods of getting the solution. First we considered the Heitler-London method directly, supplemented by ionic states. The extension of this to more complicated molecules is the so-called valence bond method. Like the Heitler-London method, it suffers from the inconvenience of dealing with non-orthogonal functions. Nevertheless, as we have mentioned earlier, it has had a good deal of application, but in a form in which unwarranted simplifications were made. We shall discuss this method in a later section. Secondly, we used the configuration interaction method as applied to determinantal combinations of molecular orbitals. This method forms the main topic of the present chapter, and it seems from most points of view to be the most generally useful way to attack molecular problems. Thirdly, we set up orthogonalized atomic orbitals, orbitals localized on the two atoms, as the atomic orbitals were, but orthogonal to each other. This forms a very simple example of a method which has certain applications both in more complicated molecules and solids. In solids, as we have mentioned, the generalization involves the Wannier functions, which we shall come to when we discuss crystalline problems. Here it is very similar to the method of equivalent orbitals, proposed by Lennard-Jones and others, which in some ways is an outgrowth of the method of directed orbitals proposed many years ago by the present writer and by Pauling. These methods are of some importance, and we shall take them up in a later section. Before going on to these more specialized topics, however, we shall proceed with our main task, the discussion of the problem of configuration interaction by means of the molecular orbital method. There has not been enough work done by this method for an extensive historical survey to be appropriate. Rather, we shall plunge right into the problems, mentioning work which has been already done as we come to it. As in the preceding chapter, we shall give our discussion largely by taking up individual cases, and we shall find that many of the cases handled in the preceding chapter are good ones for the present purpose as well. Before going on to special cases, however, we shall indicate the way in which our study of the symmetry properties of the molecular orbitals can help us in the solution of the problem of configuration interaction.

1. Symmetry Properties of Wave Functions and Configuration Interaction

Our problem in the present chapter has a very close analogy to that of the theory of complex atomic spectra, as taken up in Chapter 1. There we started with atomic orbitals of special types: they were solutions of the central field problem in which the component of angular momentum along a fixed axis was quantized, as well as the magnitude of the angular momentum. We then found that the operators representing the component of the total orbital angular momentum of the electrons along the axis, and the magnitude of this total orbital angular momentum, commuted with the energy, and hence these quantities formed diagonal matrices. We also found that the components of angular momentum at right angles to the axis commuted with the energy, but not with each other. From this we inferred a degeneracy in the problem. By diagonalizing the suitable operators, we found that we could factor our secular equation extensively, so that the final problem of solving it was not nearly as difficult as it would have been otherwise. In a similar way we could diagonalize the total spin angular momentum and its component along the axis. When this was all done, we found that the secular equation factored, each separate problem referring only to multiplets of the same L and S values.

These results were based essentially on the fact that the total angular momentum vectors for the atom satisfied the same commutation relations as the corresponding quantities for a single electron. It is now reasonable to ask if we do not have some corresponding simplification in the case of molecules. The thing which we have found to correspond to the commutation rules for the angular momentum of an atom are the commutation rules for the various symmetry operators, ordinarily reflections, rotations, and related operations, for the molecules. We now expect to find that the symmetry operations relating to a whole molecule obey the same rules as the operations relating to a single electron. It is clear from very elementary arguments that this will be the case. When we perform a symmetry operation on the electrons of a whole molecule, we of course perform identical reflections, or rotations, on the coordinates of each electron. These operations bring each electron from one point in space to another point in which the potential energy has an identical value. But now we are considering the many-electron Hamiltonian, which involves the potential energy of the various electrons in the field of the nuclei, and the coulomb interactions between the pairs of electrons, rather than the potential energy of a single electron in a self-consistent field. The potential energy in the field of the nuclei, however, will have the same symmetry as the potential energy in the self-consistent field, so that the same symmetry operations will leave either of these potential energies unchanged. Furthermore, if the whole electronic system is reflected or rotated as a rigid whole, by performing the same symmetry operations on the coordinates of each electron, the interelectronic distances will all remain unchanged, so that the total potential energy will be unchanged. Since this invariance of the potential energy under a symmetry operation was all that we had to use to show that the symmetry operations commuted with the Hamiltonian, we can carry through an identical proof in this more general case of the whole molecule.

We then find that we can diagonalize the same sort of symmetry operations for the whole molecule that we can for a single electron, and that we have the same commutation rules between the symmetry operators as for a single electron, so that we can make the same inferences about degeneracy. It becomes highly desirable, then, to set up antisymmetric wave functions which diagonalize the same symmetry operators that are diagonalized for the molecular or symmetry orbitals. We shall see, by study of the individual cases, how this can be done. In a great many cases, all that we have to do is to make our antisymmetric wave functions up out of symmetry orbitals; the corresponding symmetry operators for the molecule then become automatically diagonalized. In some cases, however, we find that there are additional symmetry operations which are not automatically diagonalized when we make up our antisymmetric functions in this way, and we must carry out an additional step to diagonalize them. In these cases, we may follow the pattern which we used in talking about complex spectra, actually find the diagonal and non-diagonal matrix components of these operators between the antisymmetric functions, and solve the resulting secular equations. We shall find a few examples of such cases.

Once we have set up these symmetrized antisymmetric wave functions (symmetrized, that is, with respect to the symmetry operations of the molecule, antisymmetric with respect to the permutations of the electrons), we need only find the matrix components of energy between these wave functions, and solve the resulting secular equation. Neither of these processes is easy. The evaluation of the matrix components of the energy involves three- and four-center integrals between atomic orbitals, assuming as in the preceding chapter that we build up our symmetry orbitals as linear combinations of atomic orbitals. These are hard enough to evaluate so that there are very few cases so far in which they have been computed. There are ways of estimating them with fair accuracy, but there are improvements being made in the straightforward calculation of such integrals, and one can hope that in the future there will really be proper calculation of the various matrix components. Then when these components have been found, the secular equation, even when we have factored it as far as possible, will often be of very high degree, and computing machines are just beginning to be able to handle the sort of secular equation which we meet. The whole subject of configuration interaction is in a stage where the first steps are being taken, and even the simplest problems seem very hard, but as the difficulties are overcome for these problems, it is to be hoped that more and more complicated molecules can be attacked.

In the cases which we shall be principally discussing, there is one considerable siplification, which is generally legitimate. We can illustrate this simplification if we assume that there are N molecular orbitals which we are considering, written as linear combinations of atomic orbitals, and n electrons in the molecule. We assume that the N orbitals are functions of spin as well as coordinates, so that each function of coordinates counts as two functions of spin and coordinates. Then we can form configurations from these N molecular orbitals in $N!/\left[n!(N-n)!\right]$ ways. This number unfortunately is generally very large, which is what leads to the difficulty of the method. Quite aside from that, however, there is a very important theorem relating to these configurations. It is the following. If we form N orthogonal linear combinations of the original N orbitals, set up the $N!/\left[n!(N-n)!\right]$ configurations formed from these new orbitals, then the antisymmetric determinantal functions formed from these new orbitals are linear combinations of those formed from the original orbitals. Hence, any function which can be written as a linear combination of the first set of determinants will be expressed equally well as a linear combination of the second set, so that if we solve our secular problem, first using one set of determinants, then using the other, the final result will be the same in either case.

In other words, if we have a set of symmetry orbitals, from which we could get molecular orbitals by the solution of a one-electron secular problem, as discussed in the preceding chapter, we could make antisymmetric functions either out of the symmetry orbitals, or out of the molecular orbitals, and the final answer would be the same, no matter which we used. Under the circumstances, since the final combination of determinants is what we desire, it is generally not necessary in such a case to determine the molecular orbitals at all. This then can be a considerable saving of effort, so that although the method of configuration interaction is a good deal more tedious than the method of molecular orbitals, it may not be quite as much worse as one would suppose.

In many cases, however, the number of configurations $N!/\left[n!(N-n)!\right]$ which could be formed from all the symmetry orbitals is so great that we cannot possibly handle all of them, and we omit many of them from our discussion. In such a case, if we use only a few of the configurations, and hope that the correct wave functions can be made up fairly accurately from them, then clearly we cannot use our theorem to avoid the requirement of setting up molecular orbitals. The extreme case of this, of course, is the molecular orbital method itself, where, as this method was interpreted in the preceding chapter, we use only one determinant. Sometimes, even in this case, however, we can make partial use of the theorem. Thus some of the configurations would arise from taking electrons from the inner shells of the atoms, and putting them in the outer molecular orbitals. Such determinantal functions would correspond to very high diagonal energies, corresponding to an x-ray excitation, and for this reason we may expect that they will appear in the final solution with very small coefficients. We shall not make any serious error if we disregard them entirely. We may then interpret the number of orbitals N which we use in computing the number of configurations, and the number n of electrons to be used in them, simply as the number of orbitals and electrons outside the closed shells of the atoms. For the electrons in these closed shells, we could use merely the symmetry orbitals. Or we could go even further: on account of the approximate non-overlap of the inner atomic orbitals on different atoms, we could use the original atomic orbitals in setting up our determinantal functions, and the results would still be substantially the same as if we had used molecular orbitals. In the simple cases which we shall discuss later in this chapter, where we are dealing mostly with very light atoms, it is generally only the 1s electron which is handled in this way, but in some cases the 2s has also been regarded as an inner electron, as compared with 2p. This approximation for the 1s is presumably justified, but for the 2s it is rather more questionable.

2. Diatomic Molecules; the Oxygen Molecule

Rather than go further with our general remarks, let us now proceed with special cases. The diatomic molecule is of course the one about which most work has been done, and we start with it. Here we have already noted that one of the symmetry operations works as with atoms. That is, the total component of angular momentum along the axis of all electrons is constant. From what we have seen in an earlier section, we see that the corresponding symmetry operation is an infinitesimal rotation about this axis. Also there is another symmetry operation: reflection in a plane passing through the axis of the molecule. And in the case of a symmetrical molecule, there are additional symmetry operations: reflection in the plane normal to the axis passing through the center of the molecule, and inversion in this center of symmetry. Let us consider which of these operations commute; at the time when we were discussing diatomic molecules in the preceding chapter, we had not yet developed our concept of the commutation of symmetry operations, and hence did not discuss this question.

We can answer our question very easily by writing the operations in analytic form. If we use spherical polar coordinates, with the axis along the axis of the line of the molecule, and the origin at the center of inversion (if there is one), the infinitesimal rotation corresponds to changing the coordinates r, θ, ϕ into $r, \theta, \phi + \Delta\phi$. Reflection in the plane $\phi = 0$, which is typical of planes passing through the axis, changes r, θ, ϕ into $r, \theta, -\phi$. Reflection in the mid-plane changes r, θ, ϕ into $r, \pi - \theta, \phi$. And inversion changes r, θ, ϕ into $r, \pi - \theta, \phi + \pi$. That is, inversion is a combination of reflection in the mid-plane, and rotation through π. It is clear from this that reflection in the plane $\phi = 0$ does not commute with rotation through $\Delta\phi$. If we rotate first, then reflect, we change r, θ, ϕ into $r, \theta, -\phi - \Delta\phi$, whereas if we reflect first, then rotate, we change r, θ, ϕ into $r, \theta, -\phi + \Delta\phi$. There is one exceptional case, however: if the wave function is independent of ϕ, neither of these operations does anything to it, and it obviously makes no difference which order we perform them in. A wave function independent of ϕ represents a Σ state, and we see therefore that for such a state, reflection in a plane such as $\phi = 0$ commutes with the rotation, and hence can be simultaneously diagonalized. Being a reflection, for which two successive performances of the same operation result in identity, the eigenvalues of the operation must be ± 1. In other words the wave function connected with a $\sum$ state will be either symmetric or antisymmetric under such a reflection. At first sight it seems paradoxical that we could have antisymmetry under such conditions, but we shall shortly find cases where we do, and the implications of this type of operation will become clearer. A $\sum$ state which is symmetric on reflection is denoted as a $\sum^+$ state, one which is antisymmetric as a $\sum^-$. There is no corresponding symmetry for anything but a $\sum$ state.

Just as the components of angular momentum of the individual electrons along the axis are denoted by the symbols σ, π, δ, etc., we have already seen that the corresponding components of angular momentum of the whole molecule are denoted by Σ, Π, Δ, etc. The standard notation for the quantum number measuring the component of angular momentum along the axis, which is 0 for σ states, ± 1 for π's, etc., is λ, though we have often denoted it by m, and the corresponding quantum number for the molecule as a whole is Λ. If we build up a determinantal function from molecular orbitals, we see at once that Λ equals the sum of the λ's of all the orbitals, just as in an atomic problem M_L equals the sum of the m_l's of all orbitals. To see this in a straightforward and analytic way, we note that one of the products from which the determinant is formed will contain the factor $e^{i\lambda_1\phi_1} e^{i\lambda_2\phi_2} e^{i\lambda_3\phi_3}$ . . . , where λ_1, λ_2, etc., are the λ's associated with the various orbitals, and ϕ_1, ϕ_2, . . . are the corresponding coordinates. When we rotate the whole system through an angle $\Delta\phi$, this means that ϕ_1, ϕ_2, . . . are each increased by this same angle $\Delta\phi$. Thus the exponential is multiplied by the factor $e^{i(\lambda_1 + \lambda_2 + \ldots)\Delta\phi} = e^{i\Lambda\Delta\phi}$, where Λ is the sum of the λ's. We see, in other words, that if we build up our determinantal function out of molecular orbitals, the resulting function will automatically diagonalize the rotation around the axis. On the other hand, we verify the fact that our function will not ordinarily diagonalize the reflection operation. Since this changes each ϕ into its negative, it will change the factor $e^{i\lambda_1\phi_1} e^{i\lambda_2\phi_2}$ . . . into $e^{-i\lambda_1\phi_1} e^{-i\lambda_2\phi_2}$ . . . , which is certainly not a constant times the original function. On the other hand, the new function is certainly degenerate with the original one, so that we see that in complete molecules, as in molecular orbitals, there will be degeneracy between the state with a given value of Λ, and that with its negative.

From this dependence on angle, we can now understand the situation involved in the $\sum^+$ and $\sum^-$ states better. We can build up a $\sum$ state out of orbitals which are not themselves σ orbitals; we need merely have the sum of the λ's equal to zero. Thus we see that in a $\sum$ state, just as in others, the reflection operation can transform a function with a factor $e^{i\lambda_1\phi_1} e^{i\lambda_2\phi_2}$ . . . into one with a factor $e^{-i\lambda_1\phi_1} e^{-i\lambda_2\phi_2}$ . . . Now, however, in contrast to the earlier case where Λ is different from zero, this new state does not correspond to a different symmetry type from the original one; the energy can have non-diagonal matrix components between the two states. Since the two states are degenerate with each other, the result will be that the suitable linear combinations to use are the sum and difference of these determinantal functions. The sum will then involve the factor $\cos(\lambda_1\phi_1 + \lambda_2\phi_2 \ldots)$, which is unchanged when all the ϕ's change into their negatives, and the difference will involve the factor

$\sin(\lambda_1\phi_1 + \lambda_2\phi_2 \ldots)$, which is antisymmetric on reflection. The first combination, in other words, corresponds to a $\sum^+$ state of the molecule, the second to a $\sum^-$ state. It is of course obvious that in a determinantal function formed entirely from σ molecular orbitals, where there is no exponential factor expressing dependence on angle, this degeneracy cannot arise, and the state is automatically a $\sum^+$ state.

In case the molecule is symmetric about a mid-point, there will be the symmetry operations of reflection in the mid-plane, and inversion changing r, θ, ϕ into r, $\pi - \theta$, ϕ, or r, $\pi - \theta$, $\phi + \pi$ respectively, as we have seen. These operations, as we can see by inspection, commute with the rotation through an angle $\Delta\phi$. Thus in such a case we can diagonalize the reflection and the inversion, and the eigenvalues of these operations will be ± 1. As in the molecular orbital, the usual convention is to describe a state which is symmetric under the inversion operation as a g state, one which is antisymmetric as a u state. It is now obvious that if we make up a determinantal wave function out of molecular orbitals each of which is g or u in its symmetry, the determinantal function will be automatically diagonalized with respect to the inversion. This inversion will change the sign of each u orbital which appears in the determinant, leaving each g orbital unchanged, so that a determinant formed from an even number of u orbitals will have g symmetry, one formed from an odd number will have u symmetry.

This completes the study of the symmetry properties of the determinantal wave functions. There is still one aspect of the problem to consider, however: the spin. This was trivial in the one-electron problem, but here we must consider it. We can, however, handle it entirely independently of the orbital symmetry properties. Thus let us consider a given choice of n spin-orbital one-electron functions, chosen from the total number of N such functions. In this set of n functions, we shall find some functions of coordinates alone which are occupied by two electrons, one of each spin; some occupied by one electron. If there are N' occupied by one electron, we can imagine other determinants in which each function of coordinates is occupied by the same number of electrons as in the determinant already considered, but in which one or more of the electrons may have the other spin. Clearly there are $2^{N'}$ such determinants, differing only in spin. The problem of degeneracy between these $2^{N'}$ states is the ordinary problem of spin degeneracy, which can be carried through just as in the atomic case. That is, we can set up the matrix components of the quantity $S_x^2 + S_y^2 + S_z^2$ between these functions, and diagonalize it, so as to get separate combinations of determinants, each combination corresponding to a definite multiplicity. We know that the Hamiltonian has no non-diagonal matrix components of energy between functions of different multiplicity. Thus this process of setting up linear combinations of determinants automatically factors our secular equation, allowing us to treat states of different multiplicities independently of each other.

In such a problem of spin degeneracy, each determinantal wave function is composed of the same orbitals as far as the coordinates are concerned, so that the combination of determinants which diagonalizes the magnitude of the spin, or which corresponds to a definite multiplicity, will also diagonalize the symmetry operations of rotation and inversion. Thus we have secured as much factoring of the secular equation as possible: we have separated the states of each multiplicity, and of each type of symmetry as far as the coordinates are concerned. From that point on, we must really solve secular equations between the various states of the same multiplicity and symmetry.

This procedure will now become much clearer if we go through an actual case in detail. We shall take the case of O_2, in which a careful study of configuration interaction has been made by Meckler.$^{(1)}$ We have already discussed this case from the standpoint of molecular orbital theory, but now we wish to go into it a good deal more thoroughly. First we remind ourselves of the symmetry orbitals of this problem, as taken up in Section 3, Chapter 3. We have σ_g and σ_u orbitals formed from the 1s atomic orbitals, σ_g and σ_u formed from the 2s atomic orbitals, σ_g and σ_u formed from the 2p's, and $\pi_{\pm g}$ and $\pi_{\pm u}$ formed from the 2p's. We should expect the σ_g molecular orbitals to consist of one almost exactly formed from the 1s orbitals, one largely formed from 2s but partly from 2p, and one largely from 2p but somewhat from 2s. Meckler disregards this probable mixture, assuming that one molecular orbital is identical with the symmetry orbital formed from the atomic 2s orbitals, but orthogonalized to the 1s, and he assumes that this molecular orbital is occupied by electrons of both spins, in all configurations which he considers. Similarly he considers that there is one molecular orbital of σ_u type formed entirely from the 2s, and always occupied. We are then left with the following molecular orbitals which will not always be occupied: the σ_g and σ_u formed from the atomic 2p's, and the $\pi_{\pm g}$, $\pi_{\pm u}$. This gives us six molecular orbitals, which combined with the two spins gives twelve, to be occupied by the eight electrons which are not accomodated in the orbitals formed from the 1s and 2s atomic orbitals. The number of configurations to be considered is then $12!/8!4! = 495$. It is obvious that without the factoring arising from symmetry and multiplicity it would be hopeless to solve the resulting secular equation.

We shall not consider all 495 of these states in our analysis of the symmetry, though the methods we shall use are typical of those required for the complete problem. The ground state is known to be of the form ${}^3\Sigma_g^-$, and another particularly interesting state is the ${}^1\Sigma_g^+$, which lies somewhat above it. We shall carry through the complete discussion of the configurations entering into these two states, and this will sufficiently illustrate the method. As a first step, let us consider what symmetries of molecular orbitals must enter into any Σ_g state; when we have done that, we shall next consider the multiplicity problem. For a Σ state, the sum of the λ values of the various molecular orbitals must be zero. For a g state, we must have an even number of u orbitals, and hence an even number of g's. A little re-

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[1] A. Meckler, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., July 15, 1952

flection will show us that this can be achieved only in the twelve ways listed in Table VIII.

Table VIII

Number of Electrons Occupying Each Molecular Orbital in O_2

Number of State	π_{+g}	π_{-g}	π_{+u}	π_{-u}	σ_g	σ_u
1	2	2	2	2		
2	2	2			2	2
3			2	2	2	2
4	2			2	2	2
5		2	2		2	2
6	1	1	2	2	2	
7	1	1	2	2		2
8	2	2	1	1	2	
9	2	2	1	1		2
10	1	1	1	1	2	2
11	1	2	2	1	1	1
12	2	1	1	2	1	1

Here we give the number of electrons occupying each of the molecular orbitals, in each of the twelve assignments of electrons to orbitals. We readily verify that each of these assignments satisfies our two conditions: the sum of the λ values is zero, or there are equal numbers of electrons in + or - states; and there are an even number of electrons in u states.

Now we must see how the spin degeneracy affects the problem. First, as a matter of curiosity, let us see how many of our 495 determinantal functions are included among those of Table VIII. In the states numbered 1 to 5 in Table VIII, there are no orbitals with only one electron, and hence no spin degeneracy; each of these leads only to a singlet. In the states numbered 6 through 9, there are two orbitals each containing one electron, so that each leads to $2^2 = 4$ determinants, giving of course a singlet and triplet. The states numbered 10 through 12 have four orbitals each containing one electron, so that each leads to $2^4 = 16$ determinants, which by the usual vector model for a four-electron problem result in a quintet, three triplets, and two singlets. Thus our table includes 5 + 16 + 48 = 69 of the 495 determinants of the problem, and will lead to 15 singlets, 13 triplets, and 3 quintets. We must next examine in detail the nature of the singlets and triplets, which alone we shall consider, and find which ones of these have the symmetries ${}^1\Sigma_g^+$, ${}^3\Sigma_g^-$, which are the only ones we are working out. This demands that we examine the wave functions in detail, to see which ones are Σ^+ and which ones are Σ^-, since this is the only remaining distinction which can help in factoring the secular equation.

When we reflect in the plane $\phi = 0$, the symmetry operation involved in the distinction between $\sum^+$ and $\sum^-$, a function π_+ changes into π_-, and vice versa. Let us consider what this does to a singlet state like that represented by the determinant formed from state 1 of Table VIII. The original determinant has as the elements of its first row the quantities

$$\pi_{+g}(1)\alpha(1)\ \pi_{+g}(1)\beta(1)\ \pi_{-g}(1)\alpha(1)\ \pi_{-g}(1)\beta(1)\ .\ .\ .$$

The effect of changing π_+ into π_-, and vice versa, is to interchange columns in this determinant. For instance, it will interchange the first and third columns, and the second and fourth, if they are arranged as shown, with corresponding interchanges among the columns containing the π_u's. Clearly this will require an even number of interchanges. But a determinant is not affected by an even number of interchanges of its rows or columns, and hence the wave function is unchanged by reflection in the plane $\phi = 0$, so that the state 1 of Table VIII represents a ${}^1\sum_g^+$ state. The same thing is true of states 2 and 3 in Table VIII.

The situation is quite different, however, for states 4 and 5 of Table VIII. It is clear that if π_+'s change into π_-'s and vice versa, the state 4 will be transformed into 5, and 5 into 4. In other words, these determinantal functions as they stand are not eigenfunctions of this reflection. They are, however, obviously degenerate with each other, and we should expect that the proper linear combinations of them to diagonalize the reflection would be their sum and difference. We could check this, if we desired, by finding the non-diagonal matrix component of the reflection operator between them, which would clearly be unity, since this operator operating on function 4 leads to 5, and operating on 5 leads to 4. A secular equation diagonalizing an operator which has no diagonal matrix components, but non-diagonal matrix components of unity, will always lead to the sum and difference of the original functions as the new eigenfunctions, and the eigenvalues will be plus and minus the non-diagonal matrix components. In other words, of the two resulting eigenfunctions, the sum and difference of 4 and 5 (properly normalized), one will have an eigenvalue of unity under the reflection operation, and will hence correspond to a ${}^1\sum_g^+$, while the other will have an eigenvalue of - 1, and will hence be a ${}^1\sum_g^-$. From the two determinantal functions 4 and 5, then, we get only one ${}^1\sum_g^+$ state.

Next let us consider the determinantal functions formed from state 6 of Table VIII. There will be, as we remember, four such determinants, representing a singlet and a triplet. From what we have just seen, the orbitals π_{+u} and π_{-u}, each occupied by two electrons, will not lead to any change in the determinant when we perform the reflection, so that the only orbitals we have to consider are the π_{+g} and π_{-g}, each occupied by one electron only, and the problem is just like a two-electron one as far as the symmetry is concerned. When we perform the diagonalization of spin, we know that the orbital part of the wave function associated with the triplet state will be of the form $\pi_{+g}(1)\,\pi_{-g}(2) - \pi_{-g}(1)\,\pi_{+g}(2)$, which clearly transforms into its negative if π_+ and π_- are interchanged. Thus this state is a ${}^3\sum_g^-$, the type we are considering. On the other hand, for the singlet state, the orbital part of the wave function will have the form $\pi_{+g}(1)\,\pi_{-g}(2) + \pi_{-g}(1)\,\pi_{+g}(2)$, which transforms into itself, leading to a

$^1\Sigma_g^+$, again of the type we are considering. The same situation holds for the singlets and triplets formed from states 7, 8, and 9 of Table VIII.

The determinants formed from state 10 of Table VIII are a good deal more complicated. They lead, as we have mentioned, to a quintet, three triplets, and two singlets, and we must examine the actual form of their wave functions before we can state their symmetry properties with respect to the reflection. This demands knowing the wave functions of the various multiplets arising in the problem of spin degeneracy of four non-equivalent electrons. We have solved the similar but somewhat simpler problem of three electrons in Eqs. (1.10) -- (1.12) of Chapter 1. The same methods serve easily to solve the problem of four electrons, and we shall merely state the results. We start with four non-equivalent orbitals a, b, c, and d, with one electron, of either spin, in each, and solve the problem of degeneracy between the 16 determinants arising from the various possible assignments of spin. We write the resulting wave functions in the following way. First, we know that each of the resulting multiplets will have a component connected with $M_S = 0$, so that we can get complete information about the properties of the wave functions by considering only this problem, with its six determinants out of the total of sixteen. Let us denote these determinants according to the listing of Table IX. Then we can represent any one of the resulting functions as linear combinations of the states 1 -- 6, with coefficients $T_1, T_2, \ldots T_6$.

Table IX

States of $M_S = 0$, Spin Degeneracy of Four Electrons

Number of State	a	b	c	d
1	+	+	-	-
2	+	-	+	-
3	+	-	-	+
4	-	+	+	-
5	-	+	-	+
6	-	-	+	+

We then find that the wave function of the quintet is represented by the combination $T_1 = T_2 = T_3 = T_4 = T_5 = T_6$. For the three triplets, the following equations must be satisfied: $T_1 + T_6 = 0$, $T_2 + T_5 = 0$, $T_3 + T_4 = 0$. In other words, we can set up the three combinations 1 - 6, 2 - 5, and 3 - 4, of the functions 1 -- 6, and the triplet functions must be linear combinations of these three functions. On account of the three-fold degeneracy, we can determine the correct combinations only by solving a secular equation for the energy. For the two singlets, we must have four equations satisfied: $T_1 = T_6$, $T_2 = T_5$, $T_3 = T_4$, $T_1 + T_2 + T_3 = 0$. That is, we can set up the three combinations 1 + 6, 2 + 5, 3 + 4, and any two linear combinations of these which are orthogonal to the quintet function, which is the sum of the three, can be taken as singlet functions. Here again the secular equation for the energy must be solved to get the correct combinations.

It is now clear that to study the symmetry properties of our functions formed from state 10 of Table VIII, we must first identify the functions a, b, c, d of Table IX with the functions π_{+g}, π_{-g}, π_{+u}, π_{-u} of Table VIII, and then must consider the symmetry of such combinations as 1 ± 6, 2 ± 5, and 3 ± 4, of the functions of Table IX. The function 1 has a determinant whose first row contains the terms $\pi_{+g}(1)\alpha(1)\ \pi_{-g}(1)\alpha(1)\ \pi_{+u}(1)\beta(1)\ \pi_{-u}(1)\beta(1)$. When we reflect in the plane $\phi = 0$, the first two columns change place, the third and fourth columns change place, and the determinant as a whole is unchanged. The same thing is true of the function 6. In other words, both combinations 1 ± 6 are of the type Σ^{+}.

The situation is quite different with the combinations 2 ± 5. The first row of the determinant representing function 2 of Table IX is $\pi_{+g}(1)\alpha(1)\ \pi_{-g}(1)\beta(1)\ \pi_{+u}(1)\alpha(1)\ \pi_{-u}(1)\beta(1)$, and for function 5 we have the same thing with α and β interchanged. When we reflect in the plane $\phi = 0$, function 2 changes into 5, and vice versa. Thus the sum 2 + 5 changes into itself, but the difference 2 - 5 changes into 5 - 2, or into its negative. The same situation holds with the combinations 3 ± 4. Putting this information together, then, we see that the function 1 - 6 represents the only ${}^3\Sigma_g^+$ which we have from our state 10 of Table VIII. The two combinations of the quantities 2 - 5 and 3 - 4 represent two ${}^3\Sigma_g^-$'s. And the two combinations of the three quantities 1 + 6, 2 + 5, and 3 + 4 which represent singlets are both of the ${}^1\Sigma_g^+$ type. From state 10 of Table VIII, then, we have two ${}^3\Sigma_g^-$'s, and two ${}^1\Sigma_g^+$'s, to add to the list of those which we are interested in.

Now let us consider the states 11 and 12 of Table VIII. As we examine their nature, we see that reflection in the plane $\phi = 0$ will transform one into the other. That is, we can set up the one quintet, three triplets, and two singlets arising from 11, and the similar multiplets arising from 12, and reflection in the plane $\phi = 0$ will transform each function of type 11 to the corresponding one of type 12. We then have a problem of degeneracy, just as we did with the states 4 and 5 of Table VIII. We shall have to take sums and differences of the various states formed from 11 and 12 of Table VIII, and in each case the sum will lead to a Σ^{+} function, the difference to Σ^{-}. Thus from the states 11 and 12 of Table IX, we shall find three ${}^3\Sigma_g^-$ states, and two ${}^1\Sigma_g^+$ states, in addition to other states whose symmetry we are not considering.

We can now survey the whole situation, and see how many states of the desired symmetry we have in all. Of the ${}^3\Sigma_g^-$ states, we have one each from states 6, 7, 8, and 9 of Table VIII, two from state 10, and three from the combination of states 11 and 12, or nine in all. Of the ${}^1\Sigma_g^+$'s, we have one each from states 1, 2, and 3 of Table VIII, one from the combination of 4 and 5, one each from 6, 7, 8, and 9, two from 10, and two from the combination of 11 and 12, or twelve in all. Thus we must solve a secular equation of nine rows and columns for the ${}^3\Sigma_g^-$ states, and one of twelve rows and columns for the ${}^1\Sigma_g^+$ states. Meckler, in the reference cited earlier, has set up the appropriate functions in the manner we have been describing, has found the matrix components of energy between them, and has solved these secular equations for a number of internuclear distances, obtaining the various energy levels, and the wave functions of the states of the desired symmetry as linear combinations of the unperturbed wave functions.

Let us now consider some properties of the solutions, as Meckler has found them. In the first place, the electronic configuration which we arrived at from the molecular orbital theory in the preceding chapter, as representing the ground state of the molecule, is that labelled 6 in Table VIII. This leads to a $^3\Sigma_g^-$ and a $^1\Sigma_g^+$ state, as we have already seen, and the triplet must lie lower. The reason why Meckler chose these two symmetry types to investigate is obvious from this: he wanted to see how much the predictions of the simple molecular orbital theory are affected by configuration interaction. It is clear that in this problem, which does not have a singlet arising from a closed shell for its ground state, even the simplest molecular orbital theory must take into account some interaction of determinants, enough to build up the proper type of function out of configuration 6 of Table VIII to represent the proper multiplicity. As in the hydrogen molecule, the molecular orbital state by itself forms a moderately good representation of the correct ground state at the observed internuclear distance, but is entirely wrong at infinite distance. This can be seen in several ways from the results of Meckler. In the first place, as far as the energy is concerned, the ground state which he finds, the lowest $^3\Sigma_g^-$ state, agrees very well with observation, having its minimum at just about the right internuclear distance, and giving a dissociation energy, and a vibration frequency around the minimum, in good agreement with experiment. On the other hand, the diagonal energy of the molecular orbital state corresponds to only about a half of the correct binding energy, and goes to a very much too high value at infinite separation. This situation is something like that shown in Fig. 2, Chapter 2, where H_{11} represents the diagonal energy of the molecular orbital state, $^1\Sigma_{g1}$ the energy of the ground state; only for oxygen the discrepancy between the two energies is a good deal greater than in hydrogen.

Another way to see to what extent the molecular orbital state represents the correct ground state is to find the coefficient by which this molecular orbital function is multiplied, when we expand the correct ground state as a linear combination of the nine $^3\Sigma_g^-$ states. This coefficient, as a function of internuclear distance, is given in Table X. The correct internuclear distance is about 2.28 atomic units, and we see that there the coefficient of the molecular orbital function is something like .97, its square being .94, so that the squares of the coefficients multiplying all other functions can only be about 0.06. Here, in other words, the molecular orbital function is rather good, though the admixture of other functions is very necessary to get a good value for the energy. But as the distance increases, there is a very rapid change in the coefficient, over to the value $0.3536 = (8)^{-1/2}$ which it has at infinity. In other words, at infinite separation the molecular orbital state by itself is no approximation at all to the ground state.

This situation is similar in principle to what we found with hydrogen, where at infinite

Table X

Coefficient Multiplying Molecular Orbital Wave Function in Expansion of Correct Ground State

Internuclear Distance	Coefficient
1.5 a.u.	0.9957
2.0	0.9848
2.5	0.9668
4.0	0.4361
6.0	0.3538
9.0	0.3536
∞	0.3536

separation there were two states making up the ground state, with equal coefficients: the molecular orbital state, in which both electrons were in the symmetric orbital a + b, and that in which both electrons were in the antisymmetric orbital a - b. Here, however, the situation is much more complicated, and we shall not go through the details of showing the connection between the molecular orbital state and the atomic multiplets. Meckler shows that at infinite distance the ground state is a combination of states 6, 7, 8, and 9, of Table VIII, all with coefficients $\pm(8)^{-1/2}$, and of two of the three triplets formed from states 11 and 12, with coefficients $\pm$ 1/2. The reason for the complication is the fact that the ground state of the atom of oxygen is a ^3P, but the same configurations also lead to a ^1D and ^1S. All the combinations of these multiplets for the two atoms must be reproduced in the various states arising at infinite separation from our 495 determinantal functions. The ground state of the molecule must go into the ^3P states of the separated atoms, in which the S vectors can combine to give a singlet, triplet, and quintet, and the L vectors to give Λ values of 2, 1, 0, -1, -2, or to Σ, Π, and Δ states. The problem of analyzing all these states at infinite separation is considerable but we find that both a $^3\Sigma_g^-$ and a $^1\Sigma_g^+$ state should arise from this lowest combination of multiplets, and these are the lowest of the states of the molecule, as found by solving the ninefold and twelve-fold secular equations.

With a molecule of this sort, in other words, the states which must be considered at infinite separation, in our study of configuration interaction, include not only unionized and ionized states, as with hydrogen, but inside each of these categories they include many different combinations of atomic multiplets. And a correct treatment of configuration interaction, such as Meckler has carried out, gives each state of the molecule going at infinite separation to one of these states of the combined atoms. It is no wonder that the problem is much more complicated than with hydrogen. There is one very interesting result of this situation, which is found in Meckler's results. His energy level for the ground state, as a function of internuclear separation, rises from its minimum with increasing internuclear distance, to a maximum, which it reaches at about 4 atomic units, and then falls again to the value at infinite distance. The reason seems to be the following. The energy of the ground state appears to be rising, at distances less than 4 units, as if it were heading at infinite separation for an energy somewhere midway in the group of energy levels which would be formed from a combination of the various multiplets of the two oxygen atoms. It persists in this direction until it has risen decidedly above the ground state at infinite separation. Only then does the wave function begin to adjust itself to the correct linear combination of determinants to form the ground state at infinity. It appears that the correct linear combinations of determinantal functions to result in the atomic multiplets are of completely different type from the combinations resulting in the molecular energy levels, and that there is a rather sudden shift from one type of combination to the other type, at around this distance of 4 atomic units. Going to smaller distances, the levels spread out on account of the interaction of molecular type, while at larger distance they spread on account of the atomic type of interaction, with some contraction of the set of levels at this distance.

This behavior is shown in Fig. 6, in which the energy of all but the highest of the nine

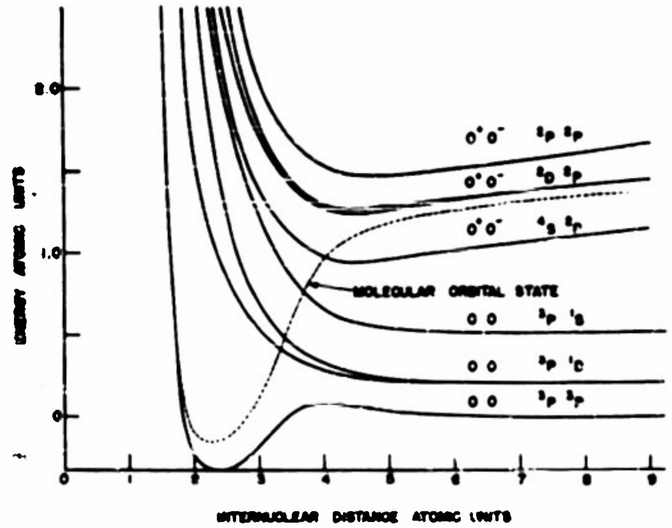

Fig. 6

Energy levels of $^3\Sigma_g^-$ states of oxygen, as function of internuclear distance, according to Meckler. Highest level, which goes to O^{++} O^{--} $^3P\,^1S$ at infinity, lies above the top of the figure. Dotted curve shows diagonal energy of molecular orbital state.

$^3\Sigma_g^-$ states is shown as a function of internuclear separation. We see the distinct contraction of the group of states around the internuclear distance 4. We also see clearly the group of four levels going to states formed from the multiplets of two neutral oxygen atoms, lying lowest at infinity; then four more states going to a combination of a positive and a negative ion. The remaining state goes to a combination of a doubly charged positive and negative ion at infinity, and lies far above the other levels shown. The dotted line in the figure indicates the molecular orbital state, which as we can see is heading approximately midway in the group of configurations formed from O^+ and O^-, as we should expect from the known partially ionic character of molecular orbital states at infinite separation.

The energies of the $^1\Sigma_g^+$ states form a diagram similar to that of Fig. 6; it would complicate the figure too much to try to plot both sets on the same figure. The lowest state of this group goes to the same energy at infinity as the lowest state of Fig. 6, but lies somewhat above it at the internuclear distance corresponding to the minimum. This lowest singlet state also has a minimum, at about the same internuclear distance as the lowest triplet, and it has a practically identical hump in the curve, the two states almost exactly coinciding in energy for distances greater than 4 atomic units. In other words, the exchange interaction which causes the splitting between singlet and triplet diminishes very rapidly as the internuclear distance increases. This fact will prove to be of interest to us in our later discussions, where we take up the problem of ferromagnetism. The oxygen molecule, which of course is paramagnetic on account of its triplet ground state, is one of the simplest examples of a magnetic substance, and its singlet-triplet separation is probably similar in its general features to the energy separations between magnetic and non-magnetic states which we find in the theory of ferromagnetism.

The case of oxygen, which we have used to illustrate the configuration interaction in diatomic molecules, is particularly complicated. To show that all cases are not so difficult, we shall finish our discussion of diatomic molecules by taking the much simpler case of fluorine, which is simpler because it has a single bond, rather than the double bond of oxygen. This case has not been worked out in detail, but we can predict easily how it would go. We now have ten electrons in the states shown in Table VIII, rather than the eight in oxygen, and again we presume that the ground state will be a Σ_g state, in this case $^1\Sigma_g^+$, since this is the symmetry type of the molecular orbital solution. We show in Table XI the various states

Table XI

Number of Electrons Occupying Each Molecular Orbital in F_2

Number of State	π_{+g}	π_{-g}	π_{+u}	π_{-u}	σ_g	σ_u
1	2	2	2	2	2	
2	2	2	2	2		2
3	2	2	2	2	1	1
4	1	1	2	2	2	2
5	2	2	1	1	2	2
6	1	2	2	1	2	2
7	2	1	1	2	2	2

which could contribute to Σ states of the molecule; the problem is now simple enough so that we have given those contributing to Σ_u's as well as Σ_g's. Our state 1 is the molecular orbital state, and is of ${}^1\Sigma_g^+$ type. State 2 is of the same type, and the interaction between these two states is just like that between the two molecular orbital states in hydrogen, leading to the two ${}^1\Sigma_g^+$ states in that molecule. State 3 leads to ${}^1\Sigma_u^+$ and ${}^3\Sigma_u^+$, and is similar to the corresponding configurations in hydrogen. Here, however, we have other configurations of the same symmetry, arising from the excitation of π electrons. Thus states 4 and 5 each lead to a ${}^1\Sigma_g^+$ and ${}^3\Sigma_g^-$, in close analogy to states 6, 7, 8, and 9 of oxygen, as given in Table VIII. Finally states 6 and 7 of Table XI show the same sort of degeneracy as 11 and 12 of Table VIII. Neither one is an eigenfunction of the operation of reflecting in the plane $\phi = 0$, so that we must take sums and differences. When we do this, we find ${}^1\Sigma_u^+$, ${}^1\Sigma_u^-$, ${}^3\Sigma_u^+$, ${}^3\Sigma_u$. Thus the net result is that we have four states ${}^1\Sigma_g^+$, two ${}^3\Sigma_g^-$, two ${}^1\Sigma_u^+$, one ${}^1\Sigma_u^-$, two ${}^3\Sigma_u^+$, and one ${}^3\Sigma_u^-$. The secular equation, in other words, is factored so that no resulting secular equation will have more than four rows and columns, and the problem should be an easy one to carry through. The ground state should come as the lowest root of the four-by-four secular equation. It would be very interesting to see how this case would work out, as representing a straightforward single covalent bond, in a case more complicated than the hydrogen-hydrogen bond which we meet in H_2.

3. The Water Molecule

Next we consider the water molecule, for which the molecular orbitals have already been discussed in Chapter 3, Section 4. We remember that we chose the plane of the molecule as the yz plane, the z axis being the bisector of the angle between the OH bonds. We found that there were two symmetry operations, reflection in the yz plane and in the xz plane, which commuted with each other, so that all wave functions are either symmetric or antisymmetric on reflection in the yz plane, and similarly all are symmetric or antisymmetric on reflection in the xz plane. The molecular orbitals which were symmetric on reflection in the yz plane, or the plane of the molecule, were called σ orbitals, those which were antisymmetric were π orbitals. Among the σ orbitals, there are two symmetry types, those symmetric or antisymmetric respectively on reflection in the xz plane. Those which are symmetric are formed from the carbon 1s, 2s, and $2p_z$ orbitals, and from the sum of the two hydrogen 1s orbitals. There are thus four such molecular orbitals, of which the one with lowest energy is much like the carbon 1s, the next lowest rather like the 2s but with mixtures of the $2p_z$ and hydrogen orbitals, and the two of higher energy are largely made up of the $2p_z$ and the hydrogen orbitals, though with some mixture of the 2s. Of these last two, the highest, which is antibonding. has a node between the carbon and the hydrogens, while the lower, which is bonding, does not. In the determinantal function formed from the lowest molecular orbitals, we have six electrons occupying orbitals of this type of symmetry, filling all but the highest antibonding orbitals. In the excited configurations which we shall consider in this section, we shall assume that the two lower orbitals are occupied by two electrons each, at all times, but that the two upper orbitals can have varying number of electrons in them.

Calculations of configuration interaction in water are being made by G. F. Koster and H. C. Schweinler.(2) They are making the assumptions just mentioned, plus a further simplification: they are assuming that the lowest molecular orbital is identical with the carbon 1s orbital (which is probably justified), and furthermore that the next molecular orbital is identical with the carbon 2s, plus enough of the 1s to make them orthogonal. This latter assumption is probably not very well justified, limiting the accuracy of Koster and Schweinler's results. They would have had no more configurations if they had first determined the actual molecular orbitals; but this would have meant a good deal more work. A still further, and in this case quite large, increase in labor would have resulted if they had assumed that the 2s-like molecular orbital was not always fully occupied with two electrons; in this case they would have had many more configurations to handle.

Among the σ orbitals antisymmetric in the xz plane, we have just two, linear combinations of the carbon $2p_y$ and the difference of the two hydrogen 1s orbitals. The orbital with lower energy is bonding, and is occupied by two electrons in the molecular orbital ground state. The higher one is antibonding. In our configuration interaction, we allow any number of electrons, subject only to the exclusion principle, in these two orbitals. Finally there is the single π orbital, identical with the carbon $2p_x$, and occupied by two electrons in the molecular orbital ground state; in our configuration interaction problem we allow any number of electrons in it.

Our problem now is to count the number of interacting configurations which will lead to the ground state of the water molecule. We are assuming that four of the ten electrons are permanently located in the two lowest molecular orbitals of the type symmetrical in both x and y (we may as well call this symmetry type $g_x g_y$, to have a simple notation). The remaining six electrons are distributed among the remaining two orbitals of type $g_x g_y$; the two orbitals of type $g_x u_y$ (that is, even in x, and hence a σ orbital, but odd in y, or in reflection in the xz plane); and the one π orbital, which we could denote as $u_x g_y$, following the scheme just set up. The symmetry of the wave function of the molecule is now of an extremely simple nature. Like that of the molecular orbitals, it must be either even or odd in reflection in the yz and xz planes, and we see at once that it will be even or odd on reflection in the yz plane according as there are even or odd numbers of orbitals which have the symmetry u_x, and similarly for reflection in the xz plane. We then can read the symmetry of the wave function off from the symmetries of the individual molecular orbitals straightforwardly, without any of the complications involved in the Σ^+ and Σ^- states which we met with oxygen.

The molecular orbital ground state, having two electrons in each occupied orbital, was

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[2] G. F. Koster and H. C. Schweinler, Solid-State and Molecular Theory Group, M.I.T., Quarterly Progress Report, January 15, 1953

necessarily of symmetry g_xg_y, so that we ask how to find all other configurations of this symmetry, assuming that they will lead to the correct ground state of the molecule. We shall have such a state if and only if there are an even number (4, 2, or 0) of electrons in the g_xg_y orbitals; an even number (4, 2, or 0) in the g_xu_y; and an even number (2 or 0) in the u_xg_y. We then see that the ways of assigning the number of electrons to the various orbitals are given as in Table XII.

Table XII

Number of Electrons Occupying Each Orbital in H_2O

Number of State	g_xg_{y1}	g_xg_{y2}	g_xu_{y1}	g_xu_{y2}	u_xg_y
1	2	2	2		
2	2	2	1	1	
3	2	2		2	
4	2	2			2
5	2		2	2	
6	1	1	2	2	
7		2	2	2	
8	2		2		2
9	2		1	1	2
10	2			2	2
11	1	1	2		2
12	1	1	1	1	2
13	1	1		2	2
14		2	2		2
15		2	1	1	2
16		2		2	2
17			2	2	2

Out of the states of Table XII, each of those which has 2 or zero electrons in each orbital leads of course to a singlet state, which is the only type we are considering, since the molecular orbital state, which is numbered 8 in our table, is of this type. Each of those, like state 2 in the Table, which has two orbitals occupied by one electron each, will of course lead to a spin degeneracy problem of two electrons, resulting in a singlet and triplet, so that each of these will yield one singlet. The one remaining state, numbered 12, in which four orbitals are occupied by one electron each, will lead to a spin degeneracy problem of four electrons, which as we know leads to a quintet, three triplets, and two singlets. Hence each of the states of Table XII except that numbered 12 will yield one singlet, while number 12 will give two singlets, resulting in 18 singlet states of symmetry g_xg_y for the molecule. This tells us, then, the number of determinants which we must form, and the order of the secular equation which we must solve, to get the ground state of the water molecule.

The resulting wave function and energy levels will of course behave properly when we make any change in the nuclear positions, consistent with the assumed symmetry. That is, we can change the angle between the OH bonds, as well as changing the OH distances, provided only the distances from the oxygen to the two hydrogens remain equal. If we wished to take up the more general problem in which the two OH distances were unequal, we should lose the advantages of our symmetry, and should have a much more complicated secular equation to solve for the ground state. Our resulting wave function will behave properly in the limit of internuclear distance; that is, if both OH distances approach infinity together, though remaining equal to each other, the wave function will reduce properly to an oxygen atom in its ground state, $1s^2 2s^2 2p^4\ {}^3P$, and to two hydrogen atoms. These two atoms, in turn, provided they are far enough apart, will be in their ground state and unionized, but if they are close together, then, in principle, our solution should reduce to the solution of the hydrogen molecule problem taken up in Chapter 2. We may notice that, even though we have pointed out that Koster and Schweinler have not used the correct molecular orbitals of the 1s and 2s type, nevertheless their solutions will behave properly at infinity, for at infinite internuclear distances the molecular orbitals in question will reduce to exactly the carbon atomic orbitals.

4. The Methane Molecule

As an example of a molecule which is almost too complicated to solve by our present methods of configuration interaction, we shall work out methane, and find the number of interacting configurations leading to the ground state. Using the same sort of methods which we have been describing for O_2 and water, we shall find that we need 104 interacting configurations to describe the ground state of methane, in such a way that when the hydrogen atoms are removed to infinite distance, maintaining always the tetrahedral symmetry of the molecule, we go properly to the limiting ground state of the carbon atom, $1s^2 2s^2 2p^2\ {}^3P$, and to the ground states of the four neutral hydrogen atoms. It is clear that this is reaching the boundaries of what we can hope to calculate by straightforward methods, and we have reached these boundaries with a molecule as simple as methane. With even slightly more complicated molecules, the straightforward application of the method of configuration interaction would become completely out of the question. We bring in methane at this point, principally to give emphasis to the statements made at the end of the preceding section, regarding the necessity of finding what terms are small enough to neglect, and of setting the calculations up in such form that we can conveniently neglect these small terms.

Let us proceed to see how we find our 104 configurations for methane. In contrast to water, which was very simple, we have here the same sort of complications which we had in O_2, in a sense, only magnified to such an extent that they are a good deal harder to handle, and we shall have to build up considerably more machinery than we have used so far, to take care of the analysis. There are a number of ways to count our configurations, but the one which we shall adopt is suggested by the remark made at the end of Section 7, Chapter 3, where we were discussing the nature of the molecular orbitals for methane. We pointed out there that the methane molecule had the same number of electrons as the neon atom; that the occupied orbitals in the ground state of the molecule were closely analogous to the 1s, 2s, and 2p orbitals in the ground state of the neon atom; and that the excited molecular orbitals, which were unoccupied in the molecular orbital representation of the ground state, were closely analogous to the 3s and 3p orbitals of the neon atom. The configuration interaction which we shall consider in the present section, then, is similar to what we should have in the neon atom if we allowed any number of electrons from 1 to 8 to be excited from the 2s and 2p orbitals to the 3s and 3p orbitals. This would obviously lead to a large number of configurations. In fact, with eight electrons to be distributed among 16 orbitals (functions of coordinate and spin), we can form $16!/8!\,8! = 12,870$ determinants. Of course, these determinants will include the wave functions of a great many different types of multiplets, so that we shall not have to solve a secular equation involving anything like the total number of such functions. The ground state of a neon atom is a ^1S configuration; and a question much closer to the one which we wish to ask is, how many ^1S states can be formed from all the ways of exciting electrons from the 2s, p orbitals to the 3s, p's? This would tell us how many states combined to give the ground state, since we should only have a secular problem between states of the same type, in this case ^1S's. The number of such ^1S states is in fact of the order of magnitude of our final answer 104, but it is not equal to it. There are several features in which our problem is not equivalent to the neon problem, and we must examine them in detail before we can carry out our counting of configurations correctly.

In the first place, even if we were dealing precisely with the neon problem, it would not be correct to count all ^1S states and to say that they could all interact with each other. The reason arises from the parity of the states of the atom. The parity of an atomic state is defined to be even if the sum of the l values of all electrons in the configuration is even, and odd if the sum of l values is odd. Thus for a single electron, the S, D, etc., states have even parity, while the P, F, etc., are odd. Odd parity is generally indicated by a superscript o after the symbol of the term, even partiy by omitting the superscript, so that we should write the states of a one-electron atom as ^2S, $^2P^o$, ^2D, $^2F^o$, etc. We now notice that in complex spectra it is possible to have states of the same L value, but of different parity. Thus for instance the interaction of two p electrons in a two-electron atom will lead to S, P, and D states, all of even parity, since each of the electrons has $l = 1$. This shows that we can have a P state of even parity. Similarly the interaction of three p electrons will lead to S, P, D, and F states, all of odd parity. These examples will be enough to show the reader that in addition to ^1S levels, like the ground state of neon, we also have $^1S^o$ levels, of odd parity, arising from some of the configurations obtained when some of the 2s, p electrons are excited to 3s, p states. We shall now show that the energy has no non-diagonal matrix components between a state of even and a state of odd parity. Hence to find the number of configurations of the neon atom which interact to form the ground state, we must count only the ^1S levels arising from all the configurations, omitting the $^1S^o$ configurations.

The reason why the parity is important is that it is connected with a symmetry operator which we have for a single atom or a central field, the operation of inversion, by which x, y, z is transformed into - x, - y, - z. This operation commutes with the Hamiltonian, and with all rotations, and hence will have a diagonal matrix. Since the repetition of the operation twice in succession yields the identity, its eigenvalues must be ± 1. Now we verify immediately, by inspecting the one-electron wave functions, that the spherical harmonics corresponding to even l values are unchanged when we perform the inversion, and those corresponding to odd l values change sign. Thus a one-electron wave function of even parity is unchanged under an inversion, while one of odd parity changes sign under an inversion. When we build up a wave function for a many-electron atom, it is clear that under an inversion each one-electron function with even l will be unchanged, while each orbital with odd l will change sign. Thus the determinantal wave function, involving products of one-electron orbitals for each electron, will change sign or not under an inversion, depending on whether the parity is odd or even. Our general theorems about symmetry operators, then, will tell us that there can be no non-diagonal matrix components of energy between two states of different parity.

We may remark parenthetically that our operation of inversion is closely related to reflection, and our two types of symmetry, the S and S^o, are closely related to the Σ^+ and Σ^- which we met with the linear molecules. In the first place, rotation of 180° about a given axis, followed by inversion about a point on that axis, is equivalent to reflection in the plane passing through the point of inversion, perpendicular to the axis of rotation. Thus for instance rotation of 180° about the x axis transforms x, y, z into x, - y, - z. Inversion transforms this to - x, y, z, which is equivalent to reflection in the plane x = 0. Thus all the symmetry operations which we have described up to now in terms of reflections can equally well be described in terms of inversions and rotations. Sometimes one method of description is more convenient, sometimes the other. Now let us consider our S and S^o types of states. The characteristic of an S state is that its wave function is unchanged when any rotation is performed, and likewise is unchanged under inversion. In an S^o state, on the other hand, there is no change under any rotation, but the function changes sign under inversion. We see, then, that an S state will be unchanged when we reflect in a plane passing through the nucleus, whereas an S^o state will change sign. If now the spherical symmetry is modified to change it to the cylindrical symmetry characteristic of a linear molecule, the S wave function will be obviously modified into a Σ^+ wave function, which is independent of rotation about the axis of the molecule and unchanged on reflection in a plane passing through the axis, whereas an S^o wave function will be modified into a Σ^-, still unchanged on rotation about the axis, but changing sign on reflection. This is not the only way we can generate Σ^+ and Σ^-

states out of atomic states by changing the spherical symmetry to cylindrical, but it will illustrate the close relationship between parity and the $\sum^{\pm}$ states. We note, of course, that for a linear molecule which does not have a center of symmetry, inversion by itself is not a symmetry operator, so that the parity is not a quantity which has significance in the wave function of such a molecule.

We now understand that in the problem of the neon atom, we find the number of configurations interacting to form the ground state by counting the number of ^1S states (omitting the $^1S^o$'s). We shall see later that there are 60 such states arising from the configurations we are considering. Now we must ask, however, what are the differences between the neon atom and the tetrahedral methane molecule, in the matter of the symmetry of the states. The two problems resemble each other, but are far from identical. Let us consider just how we can pass continuously from one problem to the other, so that we can use the machinery of the vector model of the atom, which gives us an easy way to count configurations in the neon atom, to give corresponding information for the methane molecule. We may proceed as we have done earlier, in similar problems. We start with the neon atom, then allow the hydrogen nuclei to move slowly away from the carbon nucleus in the tetrahedral directions, until they reach their proper positions for the molecule. In other words, starting with the spherically symmetrical problem, we introduce a perturbation of tetrahedral symmetry. This perturbation will split the energy levels of the atom, so that each of the perturbed energy levels will have the characteristic behavior of the tetrahedral symmetry. Once the levels are split, or the degeneracy inherent in the spherical problem is removed, we may count the number of configurations of any type, and it will not change as the magnitude of the perturbation increases. In other words, if we start with the spherical problem, and introduce an infinitesimal tetrahedral perturbation, and see how it splits the multiplets of the atom, we can get our complete answer as to the number of types of multiplets of each symmetry in the methane problem.

The complete discussion of the effect of the tetrahedral perturbation on the multiplets is best given by the group theory.(3) However, we can outline these results, and make them plausible, by elementary methods. We shall start by considering the effect of an applied field of tetrahedral symmetry on a single electron which originally was in a spherical field. This is essentially equivalent to the discussion of molecular orbitals in the tetrahedral field in methane, which we have already taken up in Chapter 3; only now we must extend it to higher multiplets, and must be more systematic about our discussion. Let us start with an atomic state of a given ℓ value. We know that we have $2\ell + 1$ separate wave functions, degenerate with each other, corresponding to the different m_ℓ values from ℓ to $-\ell$, to repre-

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[3] Dr. G. F. Koster has carried through this discussion, leading to the results to be described in this section. I am much indebted to Dr. Koster for valuable discussion regarding the problem.

sent this multiplet. For $\ell = 0, 1, 2, 3, 4$, which are the only cases we prove to need in our discussion of methane, we give the angular dependence of these wave functions in Table XIII. The functions which we have tabulated are r^ℓ times the spherical harmonics of angle; and the angles are expressed in terms of cartesian coordinates x, y, z, using the relations $x = r \sin\theta \cos\phi$, $y = r \sin\theta \sin\phi$, $z = r\cos\theta$, which express the spherical polar coordinates. In other words, our functions are polynomials, which are solutions of Laplace's equation. We have not bothered to normalize these functions.

Table XIII

Spherical Harmonics Times r^ℓ for $\ell = 0, 1, 2, 3, 4$

$$\begin{aligned}
\ell = 0{:}\quad & 1 \\
\ell = 1,\ m_\ell &= \pm 1,\ x \pm iy \\
m_\ell &= 0,\ z \\
\ell = 2,\ m_\ell &= \pm 2,\ x^2 - y^2 \pm 2ixy \\
m_\ell &= \pm 1,\ z(x \pm iy) \\
m_\ell &= 0,\ r^2 - 3z^2 \\
\ell = 3,\ m_\ell &= \pm 3,\ x(x^2 - 3y^2) \pm iy(3x^2 - y^2) \\
m_\ell &= \pm 2,\ z(x^2 - y^2) \pm 2ixyz \\
m_\ell &= \pm 1,\ x(r^2 - 5z^2) \pm iy(r^2 - 5z^2) \\
m_\ell &= 0,\ z(3r^2 - 5z^2) \\
\ell = 4,\ m_\ell &= \pm 4,\ x^4 - 6x^2y^2 + y^4 \pm 4ixy(x^2 - y^2) \\
m_\ell &= \pm 3,\ xz(x^2 - 3y^2) \pm iyz(3x^2 - y^2) \\
m_\ell &= \pm 2,\ (x^2 - y^2)(r^2 - 7z^2) \pm 2ixy(r^2 - 7z^2) \\
m_\ell &= \pm 1,\ xz(3r^2 - 7z^2) \pm iyz(3r^2 - 7z^2) \\
m_\ell &= 0,\ r^4 - 10r^2z^2 + \frac{35}{3} z^4
\end{aligned}$$

We now start with any one of these ℓ values, and consider the $2\ell + 1$ wave functions associated with it. A spherically symmetrical potential will have no non-diagonal matrix components of energy between two such wave functions, but a tetrahedral perturbation will have such components. Our object is to find suitable combinations of the wave functions associated with different m_ℓ values, but the same ℓ, such that the tetrahedral perturbation will have no non-diagonal matrix components between these linear combinations. From our previous work, we know that we can greatly diminish the labor of solving the resulting secular equation if we consider all the symmetry operations characteristic of the tetrahedral structure, and if we start by making symmetry orbitals, linear combinations of the functions of different m_l value, which diagonalize as many of these symmetry operators as possible. We shall find that in the cases we are considering, this procedure will give us a complete solution of the problem, without having to use the secular equation for energy at all.

Let us first remind ourselves of what the symmetry operators are for the tetrahedral molecule; we shall be a little more complete and systematic in tabulating them than we were in Chapter 3. First, we can rotate through 180° about any one of the three two-fold axes given by the x, y, and z axes in Fig. 5. Secondly, we can rotate through ± 120° about any one of the four three-fold axes indicated by 1, 2, 3, 4 in Fig. 5. Then there are two types of reflection symmetry, which we did not stress in Chapter 3, since we did not need to use them at that time. We can reflect in one of the planes like $x = 0$, and then rotate through ± 90° about the corresponding axis like the x axis; this is an operation which we did not mention in Chapter 3. It can equally well be described as inversion, followed by rotation of ± 90° about the axes like the x axis. Fourth and last, we can reflect in one of the six planes $x = \pm y$, $y = \pm z$, $z = \pm x$. These reflections were mentioned, but not used, in Chapter 3. They can alternatively be described as rotations of 180° through any one of the six axes like $x = \pm y$, $z = 0$ (that is, the axis represented by the bisector of the angle between x and y axes), followed by an inversion. To make everything clear, we give in Table XIV the complete description of each of these types of symmetry operations, by showing the values into which the coordinates x, y, z are transformed by the various operations.

Table XIV

Transformed Values of Coordinates x, y, z, Under the Symmetry Operations of the Tetrahedron

Identity: (x, y, z)
Class I: $(x, -y, -z)$, $(-x, y, -z)$, $(-x, -y, z)$
Class II: (y, z, x), (z, x, y), $(-y, -z, x)$, $(-z, x, -y)$, $(y, -z, -x)$, $(-z, -x, y)$, $(-y, z, -x)$, $(z, -x, -y)$
Class III: $(-x, -z, y)$, $(-x, z, -y)$, $(-z, -y, x)$, $(z, -y, -x)$, $(y, -x, -z)$, $(-y, -x, z)$
Class IV: (x, z, y), $(x, -z, -y)$, (z, y, x), $(-z, y, -x)$, (y, x, z), $(-y, -x, z)$

From Table XIV, we see that, including the identity, there are twenty-four independent symmetry operations for the tetrahedron. We can check immediately that this must be the correct number, by considering the geometry of the tetrahedron, as shown in Fig. 5. Let us consider a point in space, represented by the coordinates x, y, z, and see how many other points must have the same potential, according to the tetrahedral symmetry. Thus for convenience let this point be located on the front face of the cube in Fig. 5, or on the face perpendicular to the x axis, and let it be fairly close to the atom 1. As we look at Fig. 5, we see that there must be another equivalent point in this same face, the mirror image of the first point in the line joining atoms 1 and 2. Similarly there must be two other points in the same face, located in equivalent positions with respect to atom 2. Thus in this face there are four points with equal potentials. Each of the other faces of the cube will likewise have four points equivalent to these, so that with the six faces, we have twenty-four points in all. The coordinates of these points are precisely those given in Table XIV. For future reference, we may note that if we were dealing with cubic symmetry rather than tetrahedral, so that we had atoms at all eight corners of the cube in Fig. 5, there would be twice as many points of equivalent potential; thus in the front face of the cube we should have points similarly located with respect to all four corners of the cube, rather than just near the points labelled 1 and 2 in Fig. 5. We should then have 48 equivalent points in all, and there are in fact 48 symmetry operations characterizing the cubic symmetry. The first step in discussing the symmetry operations of any problem according to the group theory is identical with what we have just done in Table XIV, to make a complete table of all the symmetry operations, and to find how many there are.

Let us now proceed, by inspection, to try to set up combinations of our spherical harmonics corresponding to different m_ℓ values, but the same ℓ, from Table XIII, which diagonalize the symmetry operations of Table XIV as far as possible. First we remind ourselves of what we did in Chapter 3. There we were interested only in s and p electrons, so that we had to consider only $\ell = 0$ and 1. For an s electron, the problem is trivial: the wave function is independent of angle, and transforms into itself under any of the 24 symmetry operations. For a p electron, the problem is not so trivial. We have to make combinations of the functions $x \pm iy$ and z from Table XIII. We remember, from our discussion of Chapter 3, that the symmetry operations of Type I, the two-fold rotations, do not commute with the operations of the other types, so that we cannot simultaneously diagonalize them. We decided to diagonalize the operations of Type I. To do this, we saw by inspection that we wanted the three functions x, y, z, which are obviously linear combinations of the three given in Table XIII. That is, remembering that the real orbitals are of the form x, y, or z times a function of r, which we called p_x, p_y, p_z, the three correct functions are p_x, p_y, p_z themselves. By inspection of Table XIV, we then see that p_x is transformed into itself by the first operation of Type I, into its negative by the second and third operations of Type I, into p_y by the first operation of Type II, p_z by the second, $-p_y$ by the third, and so on; into $-p_x$ by the first two operations of Type III, $-p_z$ by the third, p_z by the fourth; and so on. In other words, as we expected, the operations of Type I have diagonal matrices with respect to these three functions p_x, p_y, p_z, but the other operations do not.

Now let us approach a problem which we have not so far had to consider, the d electron, with $\ell = 2$. If we inspect Table XIII, we see that all five spherical harmonics for this ℓ value can be written in terms of the five quantities $x^2 - y^2$, $r^2 - 3z^2$, yz, zx, and xy. Let us now ask what effect our 24 symmetry operations have on these five functions, finding the matrix components of our symmetry operations, to see to what extent these symmetry operations are already diagonalized. The operations of Class I are already diagonalized, as we see at once: the first two functions transform into themselves, and the last three transform into

± themselves. But now we observe a further thing, when we examine the other types of symmetry operations. We find that the three functions yz, zx, and xy transform into themselves or each other under each of the symmetry operations; they never transform into the other functions $x^2 - y^2$, $r^2 - 3z^2$. Similarly these latter two functions do not transform into yz, zx, or xy. In other words, there are no non-diagonal matrix components of any of the symmetry operators between any function of the set yz, zx, xy, and either of the two in the set $x^2 - y^2$, $r^2 - 3z^2$. In the language of the group theory, the two sets of functions yz, zx, xy and $x^2 - y^2$, $r^2 - 3z^2$, form bases of two different irreducible representations of the tetrahedral group. By this we mean that no symmetry operations of the group have non-diagonal matrix components between the wave functions corresponding to two different irreducible representations; but that on the other hand it is impossible, by making linear combinations of the wave functions within one irreducible representations, to break it down into even smaller sets of wave functions between which there are no non-diagonal matrix components. If such reduction were possible, we should have a reducible representation. For instance, the five functions corresponding to $m_\ell = \pm 2, \pm 1, 0$ for $\ell = 2$, from Table XIII, with which we started, form a basis for a reducible representation of the tetrahedral group, since we can make the linear combinations we have been discussing in this paragraph, and form two irreducible representations from them. No such further reduction is possible.

The importance of irreducible representations arises from the fact that there are no non-diagonal matrix components of energy between wave functions belonging to two different irreducible representations. In other words, once we have set up linear combinations of our orbitals belonging to irreducible representations, we have automatically gone as far as we can in diagonalizing the energy, by use of the symmetry operators alone. A further property of the wave functions belonging to a single irreducible representation is that when we have diagonalized the energy completely, we shall find that the diagonal energies associated with the different wave functions contained in the same irreducible representation are equal to each other, or that we have degeneracy. In other words, the set of wave functions associated with a single irreducible representation plays the same role in a symmetry problem of a molecule which the set of wave functions associated with a single ℓ value does in the problem of atomic multiplets. In fact, the set of $2\ell + 1$ wave functions corresponding to the different m_ℓ values, for the problem of spherical symmetry, as given in Table XIII, forms the basis for an irreducible representation for that type of symmetry.

The number of separate wave functions contained in the basis for a given irreducible representation is known as the dimensionality of that irreducible representation. The matrices of the various symmetry operators have a number of rows and columns equal to this dimensionality, provided we are asking how these symmetry operators transform one of the wave functions contained in the basis for a given irreducible representation into the other functions in this same basis. We may have irreducible representations of many different dimensionalities for the same group of symmetry operations. Thus for the spherical symmetry, we have irreducible representations of dimensionality $2l + 1$, where l can be any integer, as we have just seen. In the tetrahedral group, we have found three dimensionalities so far. The s-like wave function transformed into itself under all symmetry operations. It therefore forms a one-dimensional representation, all by itself. The three functions x, y, z, or p_x, p_y, p_z, form the basis for a three-dimensional representation. The two functions $x^2 - y^2$, $r^2 - 3z^2$, form the basis for a two-dimensional representation. Finally, the three functions yz, zx, xy, form the basis for a three-dimensional representation.

We have stated without proof two properties of irreducible representations: that the energy has no non-diagonal matrix components between wave functions belonging to two different irreducible representations, and that when the energy is diagonalized, the states formed from a single irreducible representation are degenerate with each other. Let us see how we prove these properties. For the general proofs, we should use the group theory. We can, however, carry out perfectly satisfactory proofs in each special case, from symmetry properties. Thus let u_1 belong to one irreducible representation, u_2 to another. We wish to prove that $\int u_1^* Hu_2 \, dv = 0$. Surely the integral, which we may call H_{12}, will be unchanged if we perform one of our symmetry operations on the coordinates appearing in u_1, H, and u_2, for this merely changes the names of the variables of integration. This symmetry operation will leave H unchanged, by the fundamental nature of the symmetry operations, but it will make changes in u_1 and u_2 which will be of different types. For illustration, suppose u_1 belongs to the one-dimensional representation of the tetrahedral group, so that it is unchanged under any of the operations of the group. Suppose that u_2 for example is p_x. Let us consider the operation which changes x, y, z into -x, y, -z. This will leave u_1 unchanged, but will change p_x into its negative. Thus it will transform H_{12} into its negative. But we have also seen that it must leave H_{12} unchanged. Hence H_{12} must be zero. By inspection, we can see that similar proofs can be given showing that there are no non-diagonal matrix components of energy between our one-dimensional, our two-dimensional, and our three-dimensional representations of the tetrahedral group.

When we come to consider our two three-dimensional representations, however, for which the functions x, y, z, and yz, zx, xy form bases, we see that the situation is quite different. If we examine how the three functions x, y, z transform into each other under the 24 operations of the tetrahedral group, and then ask how the three functions yz, zx, xy transform into each other, we find that they transform in exactly identical ways. Thus the operation which transforms x, y, z into x, -y, -z transform the function x into itself, and likewise it transforms yz into itself; and so on for all the rest. Two sets of functions which transform into each other in identical ways under all operations of the group are considered to form two different bases for the same irreducible representation. We see at once that our proof that the non-diagonal matrix component of energy is zero between functions belonging to two irreducible representations breaks down if we have two sets of functions, like the present ones, which transform in identical ways; for then the two functions u_1 and u_2 will transform in identical ways, and we cannot find any symmetry operator, as in the last paragraph, which will change the matrix component H_{12} into its negative. In other words, there is no reason why there should not be non-diagonal matrix components of energy between a set of functions like x, y, z and a set like yz, zx, xy. As far as symmetry is concerned, they belong to an identical type of behavior.

We have now to interpret the statement that there are no non-diagonal matrix components of energy between wave functions belonging to two different irreducible representations. Let us next examine the degeneracy of the states included in a single irreducible representation. Let us assume that we have diagonalized the energy between these wave functions. Then we know that there must be some of the symmetry operators which have non-diagonal matrix components between different wave functions of our set, for we know by the fact that we are dealing with an irreducible representation that there is no possible linear transformation which will diagonalize all the symmetry operators. Let us then take two of the wave functions, say i and j, out of the set of linear combinations which diagonalize the energy. Let the diagonal matrix components of energy of these two states be E_i and E_j. Let us take a symmetry operator F which has a non-vanishing matrix component F_{ij} between these two states. Let us then write the ij component of the matrix equation HF - FH = 0, expressing the fact that F and the energy commute with each other. This contains only one term, $(E_i - E_j) F_{ij} = 0$. Since by hypothesis $F_{ij} \neq 0$, we must have $E_i = E_j$, or the states are degenerate, as we have indicated above.

Now let us see where we stand with our problem. We have found three different irreducible representations of the tetrahedral group, a one-dimensional one which is unchanged under all operations of the group, a two-dimensional one for which a basis consists of the two functions $x^2 - y^2$ and $r^2 - 3z^2$ (we have not examined how these transform into linear combinations of each other under the operations of the group, but it is easy to do so), and a three-dimensional one of which we have given two possible bases, the three functions x, y, z, or the three functions yz, zx, xy. We have shown that under a tetrahedral perturbation, an S state is not split up, but remains as a one-dimensional representation of the tetrahedral group. A P state becomes a three-dimensional representation of the tetrahedral group, and leads to a three-fold degenerate state, so that it likewise is not split by the tetrahedral perturbation. With the D state, however, the situation is quite different. The three-dimensional irreducible representation containing the three functions yz, zx, xy will lead to a three-fold degenerate level of the same symmetry as that arising from the P state, but the two-dimensional representation will be expected to result in a two-fold degenerate level having a different energy. We can see immediately from the nature of the wave functions why we expect the energy to be different for these two different types of representations. The four hydrogen atoms in methane lie at points x = y = z = a, x = - y = - z = a, - x = y = - z = a, and - x = - y = z = a. At the positions of the hydrogens, each one of the functions like yz, zx, xy will be $\pm a^2$; thus the function yz equals a^2 at atoms 1 and 2, $- a^2$ at 3 and 4.

On the other hand, the functions $x^2 - y^2$ and $r^2 - 3z^2$ are both zero at all hydrogens. It is obvious, then, that the presence of the hydrogens will perturb these two types of wave function in quite different ways.

We have now gone far enough with our general understanding of the problem so that we can go on with the cases $\ell = 3$ and $\ell = 4$. If we examine the wave functions for $\ell = 3$, we find that they can all be written as linear combinations of the following seven functions:

$$\begin{aligned}&xyz\\ &x(3r^2 - 5x^2),\ y(3r^2 - 5y^2),\ z(3r^2 - 5z^2)\ .\\ &x(y^2 - z^2),\ y(z^2 - x^2),\ z(x^2 - y^2)\ .\end{aligned}$$

The first of these, we find, transforms into itself under any of the 24 operations of the group. Thus it belongs to the same one-dimensional irreducible representation of the group as the s function. The next three transform into each other precisely like the functions x, y, z, under all operations of the group, and hence belong to the same three-dimensional irreducible representation which we have already found. The last three, however, are different. They form a basis for another three-dimensional irreducible representation, of different type from the one we have already considered. They transform in the same way as x, y, z under all rotations, but under the symmetry operations involving inversion or reflection, they transform to the negative of what the functions of the other irreducible representation would do. Thus under the operation of Class IV, in Table XIV, in which x, y, z transforms into x, z, y, the function $x(3r^2 - 5x^2)$ transforms into itself, just as x does, but $x(y^2 - z^2)$ transforms into the negative of itself. We see, then, that the seven sub-levels of an F state, with $\ell = 3$, split into three levels under a tetrahedral perturbation: a non-degenerate one transforming like an s state, a three-fold degenerate state transforming like a p state, and a second three-fold degenerate state transforming in this new way.

Similarly for $\ell = 4$ we find that we can write all of our functions in terms of the following nine:

$$\begin{aligned}&x^4 + y^4 + z^4 - 3x^2y^2 - 3y^2z^2 - 3z^2x^2\\ &x^4 - y^4 - \tfrac{6}{7}(x^2 - y^2)\, r^2,\ z^4 - \tfrac{1}{2}(x^4 + y^4) - \tfrac{6}{7}\left[z^2 - \tfrac{1}{2}(x^2 + y^2)\right] r^2\\ &yz(7x^2 - r^2),\ zx(7y^2 - r^2),\ xy(7z^2 - r^2)\\ &yz(y^2 - z^2),\ zx(z^2 - x^2),\ xy(x^2 - y^2)\ .\end{aligned}$$

Of these functions, (4) the first transforms like our one-dimensional irreducible representation, transforming into itself under any one of the symmetry operations. The next two trans-

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[4] These functions, including a number of others of higher ℓ values, are given by F. C. von der Lage and H. A. Bethe, Phys. Rev. 71, 612 (1947), in connection with a discussion of symmetry properties of cubic crystals. The cubic symmetry group is so similar to the tetrahedral group that the same types of combinations of wave functions appear in both.

form like the functions $x^2 - y^2$, $z^2 - 1/2(x^2 + y^2)$ (which is proportional to $r^2 - 3z^2$), of our two-dimensional representation. The next three transform like our three-dimensional representation transforming like x, y, z, and the last three transform like the other type of three-dimensional representation, or like $x(y^2 - z^2)$, $y(z^2 - x^2)$, $z(x^2 - y^2)$. Thus we have no new types of irreducible representations appearing in the F states.

We can show, as a matter of fact, by general methods of the group theory, that there are only five possible irreducible representations of the tetrahedral group, of which we have already found examples of four. The remaining one is a one-dimensional representation, which occurs for the first time for $\ell = 6$, for which the appropriate wave function is $x^4(y^2 - z^2) + y^4(z^2 - x^2) + z^4(x^2 - y^2)$. This wave functions transforms into itself under all those symmetry operations, of Types I and II, Table XIV, which involve only rotations; but it transforms into its negative under the operations of Types III and IV, which involve inversion as well.

The general theorem of the group theory, which leads to the information that these five irreducible representations are the only possible ones, is useful and simple in its statement, though we shall not go into its proof.(5) In the first place, it states that the number of irreducible representations for any group of operations equals the number of classes of symmetry operations. Classes of symmetry operations are defined in a precise way by the methods of group theory, but they amount to just what we have denoted by the various classes in our Table XIV. There we mentioned the operations of Classes I, II, III, and IV among the 24 symmetry operations of our tetrahedral group; the identity operation, which was not included in any of these four classes, forms a class by itself, so that we have five classes and the general theorem states that we must have five irreducible representations. Another closely related theorem tells us the dimensionality of each of these irreducible representations. This states that the sum of the squares of the dimensionalities of all irreducible representations equals the number of symmetry operations in the group. In our case, where there are five irreducible representations, and 24 symmetry operations, the sum of the squares of the dimensionalities must equal 24. The only integers which can satisfy these conditions are 1, 1, 2, 3, 3, which satisfy the equation $1^2 + 1^2 + 2^2 + 3^2 + 3^2 = 24$. These simple but powerful theorems thus allow us at once to predict the number and dimensionalities of the irreducible representations which we find in the present case.

It is now convenient to have a notation for our five types of irreducible representation. It is customary to denote irreducible representations by the symbol Γ, with a subscript to number the individual representation (the subscripts will be different, therefore, for different types of symmetry). Let us number the five representations in order of increasing dimensionality. Thus we shall denote the irreducible representation with transformation like

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[5] For a proof, see for example Eyring, Walter, and Kimball, Quantum Chemistry (John Wiley and Sons, Inc.) 1944.

an s function, which goes into itself under any of the symmetry operations, by Γ_1. The other one-dimensional representation, with transformation like $x^4(y^2 - z^2) + y^4(z^2 - x^2) + z^4(x^2 - y^2)$, will be denoted by Γ_2. The two dimensional representation, representing the transformation of two functions like $x^2 - y^2$ and $r^2 - 3z^2$ (or $z^2 - 1/2(x^2 + y^2)$) respectively, will be called Γ_3. The three-dimensional representation whose basis consists of three functions transforming like x, y, z will be called Γ_4, and the other three-dimensional representation involving three functions transforming like $x(y^2 - z^2)$, $y(z^2 - x^2)$, $z(x^2 - y^2)$, will be called Γ_5.

In terms of this notation, we can systematize what we have found. Remembering the parity of the one-electron problem, we have found that under a tetrahedral perturbation, an atomic S state becomes a Γ_1 state of the tetrahedral symmetry. An atomic P^o becomes a Γ_4 state. An atomic D splits into a doubly degenerate Γ_3 state, and a triply degenerate Γ_4. An atomic F^o splits into a Γ_1, a Γ_4, and a Γ_5. Finally, an atomic G state splits into a Γ_1, a Γ_3, a Γ_4, and a Γ_5. We have proved these results only for a one-electron problem. However, the symmetry properties are not at all dependent on having one-electron problems. We have already pointed out that the wave function of a whole atom or molecule has exactly the same symmetry operations as that of a one-electron problem. Thus any atomic multiplet, no matter of how complicated an atom, will split in the same way, provided it has the same L value, and the same parity. We have got complete information, in other words, about the S, D, and G states of even parity, and the P and F states of odd parity. It still remains to investigate the S, D, and G states of odd parity, and the P and F of even parity.

We cannot investigate these other states by considering one-electron problems. Thus it is more complicated to handle them by inspection, though we can do it by considering two- and three-electron spectra. By the general methods of group theory, Koster has shown that an S^o state goes over into one of symmetry Γ_2 under a tetrahedral perturbation, a P into a Γ_5, a D^o into Γ_3 and Γ_5, an F into Γ_2, Γ_4, and Γ_5, and a G^o into Γ_2, Γ_3, Γ_4, and Γ_5. We shall not check all these results, but we can easily show how they come about by one or two examples. Thus the simplest several-electron problem which leads to an S^o state is that of three p electrons. If we have three equivalent p electrons, we remember that we have the multiplets $^2P^o$, $^2D^o$, $^4S^o$. We can get the orbital dependence of the S^o wave function, in which we are interested, by setting up the single determinantal wave function corresponding to a component of spin along the axis of 3/2 units, or the case in which all three electrons have the same spin, and hence must have different orbital functions. If we put one in the p_x state, one in p_y, one in p_z, the wave function will be the determinant

$$\begin{vmatrix} p_x(1) & p_x(2) & p_x(3) \\ p_y(1) & p_y(2) & p_y(3) \\ p_z(1) & p_z(2) & p_z(3) \end{vmatrix}$$

which equals $p_x(1)\,p_y(2)\,p_z(3) + p_y(1)\,p_z(2)\,p_x(3) + p_z(1)\,p_x(2)\,p_y(3) - p_z(1)\,p_y(2)\,p_x(3) - p_x(1)\,p_z(2)\,p_y(3) - p_y(1)\,p_x(2)\,p_z(3)$. We readily find that this function transforms according to the representation Γ_2 under all the symmetry operations. Thus a symmetry operation of Type I, in which $x_1, y_1, z_1, x_2, y_2, z_2, x_3, y_3, z_3$ transform into $x_1, -y_1, -z_1, x_2, -y_2, -z_2, x_3, -y_3, -z_3$, so that each p_x transforms into itself, each p_y and p_z into its negative, clearly leaves the wave function unchanged. Similarly the cyclic permutations involved in the operators of Type II leave the function unchanged. On the other hand, the operators of Type III and Type IV change its sign, as we see immediately by insepction.

In a similar way, we can check the fact that a P state transforms like Γ_5. The simplest case where such a state occurs is in the problem of two equivalent p electrons, leading to ^1S, ^1D, ^3P. Here again we can get the orbital dependence of the P state from the sublevel of maximum component of spin along the axis. Now we can set up three determinants, one formed by putting the two electrons into p_y and p_z states, one by putting them into p_z and p_x, and one by putting them into p_x and p_y. The first of these leads to the function $p_y(1)\,p_z(2) - p_z(1)\,p_y(2)$, and the other two follow from this by cyclic permutation. We readily verify that these three functions transform into each other like Γ_5. We can check the remainder of the table in similar ways.

We have now completed our task of investigating the effect of a tetrahedral perturbation on the various types of multiplets of an atom, up to $l = 4$. Let us then remember why we have been doing this. We want to be able to find all the states which combine to form the ground state of the methane molecule, with its tetrahedral symmetry. This ground state has the s-like symmetry resulting from an S state of the neon atom, as modified by the tetrahedral field. That is, as we now know, it is a $^1\Gamma_1$ state. We now see that each ^1S state of the atom will result in such a $^1\Gamma_1$ state, but that we also have such states arising from other atomic multiplets. In particular, each $^1F^o$ atomic state, and each ^1G level, will also lead to a state of the same symmetry. We can get our desired number of combining states, then, by setting up all the atomic levels arising from the various configurations which we are considering, and counting the number of ^1S, $^1F^o$, and ^1G levels arising from them. When we do this, we find 60 ^1S levels, 32 $^1F^o$'s, and 12 ^1G's, a total of 104 levels, which is the desired number. We see that the effect of imposing the tetrahedral perturbation on the original spherical symmetry has been to increase the number of combining levels from the 60 ^1S levels which we should have in Ne, to this larger number 104. This is the sort of thing which we should expect: decreasing the symmetry of a problem by a perturbation always tends to make the factoring of the secular equation on account of symmetry less effective, increasing the number of combining states. The limiting case, of course, comes when the symmetry is completely lost, a limiting case where the only remaining factoring comes from the spin degeneracy.

To clarify for the reader the method of counting the configurations, we give in Table XV the number of multiplets of the desired type arising from each of the atomic configurations

Table XV

Number of ^1S, $^1F^o$, and ^1G Levels in Configurations of Ne

Configuration	No. of ^1S	No. of $^1F^o$	No. of ^1G
$2s^2 2p^6$	1		
$2s^2 2p^5 3p$	1		
$2s 2p^6 3s$	1		
$2s^2 2p^4 3s^2$	1		
$2s^2 2p^4 3s 3p$		1	
$2s^2 2p^4 3p^2$	3		1
$2s 2p^5 3s 3p$	2		
$2s 2p^5 3p^2$		1	
$2p^6 3s^2$	1		
$2p^6 3p^2$	1		
$2s^2 2p^3 3s^2 3p$	1		
$2s^2 2p^3 3s 3p^2$		3	
$2s^2 2p^3 3p^3$	3		1
$2s 2p^4 3s^2 3p$		1	
$2s 2p^4 3s 3p^2$	4		1
$2s 2p^4 3p^3$		3	
$2p^5 3s^2 3p$	1		
$2p^5 3s 3p^2$		1	
$2p^5 3p^3$	1		
$2s^2 2p^2 3s^2 3p^2$	3		1
$2s^2 2p^2 3s 3p^3$		3	
$2s^2 2p^2 3p^4$	3		1
$2s 2p^3 3s^2 3p^2$		3	
$2s 2p^3 3s 3p^3$	6		2
$2s 2p^3 3p^4$		3	
$2p^4 3s^2 3p^2$	3		1
$2p^4 3s 3p^3$		3	
$2p^4 3p^4$	3		1
$2s^2 2p 3s^2 3p^3$	1		
$2s^2 2p 3s 3p^4$		1	
$2s^2 2p 3p^5$	1		

Table XV (con'd.)

Configuration	No. of ${}^1S$	No. of ${}^1F^o$	No. of ${}^1G$
$2s2p^2 3s^2 3p^3$		3	
$2s2p^2 3s3p^4$	4		1
$2s2p^2 3p^5$		1	
$2p^3 3s^2 3p^3$	3		1
$2p^3 3s3p^4$		3	
$2p^3 3p^5$	1		
$2s^2 3s^2 3p^4$	1		
$2s^2 3p^6$	1		
$2s2p3s^2 3p^4$		1	
$2s2p3s3p^5$	2		
$2p^2 3s^2 3p^4$	3		1
$2p^2 3s3p^5$		1	
$2p^2 3p^6$	1		
$2s3s3p^6$	1		
$2p3s^2 3p^5$	1		
$3s^2 3p^6$	1		
Total	60	32	12

of the neon atom which we are considering. The method of getting at these numbers is a perfectly straightforward application of the vector model. Thus for instance let us take the configuration $2s2p^4 3s^2 3p$. The set of four equivalent p electrons results in ${}^1S\,{}^1D\,{}^3P$. Combining this with the 3p ${}^2P^o$ gives ${}^2P^o$, ${}^2(P^oD^oF^o)$, ${}^{2,4}(S^oP^oD^o)$. The $3s^2$ ${}^1S$ has no effect on the multiplet structure. Finally combining with 2s ${}^2S$ leads to ${}^{1,3}P^o$, ${}^{1,3}(P^oD^oF^o)$, ${}^{1,3,3,5}(S^oP^oD^o)$. Among all these multiplets, we find one ${}^1F^o$, which is entered in Table XV. The other configurations are handled in just such ways.

In Table XV, we have arranged the configurations in order of the number of electrons excited to the M shell (3s, 3p) in neon. We see that there are two configurations with one excited electron, and 11 ${}^1\Gamma_1$ states arising from two excited electrons. These thirteen excited states are the only ones having non-diagonal matrix components of energy to the ground state $2s^2 2p^6$, and their diagonal energy will lie lower than that of more highly excited states. Thus it seems plausible that these thirteen states will have the next largest coefficients, next to that of the ground state $2s^2 2p^6$, in the linear combination of our 104 functions leading to the best representation of the ground state of the methane molecule. One could only establish whether this was the case, by actually carrying through the calculation of the whole problem.

CONFIGURATION INTERACTION IN MOLECULES

This is a formidable problem, but it is hoped that it will stand as a challenge, to be undertaken by somebody in the not too distant future, as the methods both of computing matrix components and of solving secular equations become better worked out.

We must point out, however, that though it is reasonable that the fourteen states which we have just mentioned should be the most important in the expansion of the ground state of the methane molecule at small internuclear distances, this is by no means true at large distances. The states which we have called 2s and 3s, for small internuclear distance, will really resemble the 2s and 3s wave functions of the neon atom, so that the one-electron energy of the 3s will lie a good deal above that of the 2s. As the nuclei of the hydrogen atoms get further apart, however, we must remember the real character of the molecular orbitals. We remember that really the function which we have called 2s is a linear combination of the carbon 2s function, and the sum of the four hydrogen 1s functions, the combination being such that the orbital has a maximum between the carbon and hydrogen atoms. The function which we have called 3s is a similar combination, but with a node between the carbon and the four hydrogens. At the actual internuclear distance, the one-electron energy of the state which we have called 3s lies well above that which we have called 2s, since the former is anti-bonding and the latter bonding. At infinite internuclear distance, however, the two states become degenerate with each other, just as the symmetric and antisymmetric molecular orbitals a ± b of the hydrogen molecule problem become degenerate with each other at infinite internuclear distance. In this limit, then, many of our 104 interacting states will reduce to the same diagonal energy, and it is no longer true that "excitation" of electrons from the 2s-like or 2p-like states to the 3s-like or 3p-like states will produce any great increase in diagonal energy. We expect, in other words, that a great many of our 104 states will appear in the correct linear combination to represent the ground state at infinite internuclear distance.

The probable state of affairs may be expected to resemble that previously described for oxygen, as calculated by Meckler. That is, at small internuclear distances we may expect the molecular orbital state $2s^2 2p^6$, probably supplemented by the thirteen other states we have mentioned, to lead to a fairly good description of the ground state of the molecule. As the internuclear distance increases, however, we may expect a complete, and rather sudden, change in the nature of the coefficients multiplying our 104 functions in the expansion of the ground state, changing over to the coefficients necessary to describe the molecule at infinite internuclear separation, with all atoms in their ground states. Very likely the lowest energy level, as a function of the internuclear distances of the carbon-hydrogen pairs, will show a hump, as in oxygen. We may expect the change in the wave function, in this region of internuclear distances, to be so profound that no simple approximation based on the combined molecule will extrapolate well to infinite internuclear distance, or conversely no treatment based on the separated atoms and their multiplets will extrapolate well to the molecule. The writer suspects that no very great simplification of the problem of the interaction of our 104 states can be made, consistent with giving a correct description of the behavior of the molecule over all internuclear distances. It seems likely, however, that if we chose just those states out of the 104 which were necessary to describe the molecule properly at infinite internuclear separation, and solved the secular problem between them, we should have a good approximation. This number is substantially less than 104, though we shall not go through the complicated problem of counting to see just how many such states there are.

5. Simplified Problems: The Ethane Molecule

The case of methane, which we have just discussed, should be enough to convince us that a complete treatment of configuration interaction is going to prove impracticable for any but the simplest molecules. It is therefore worth asking if we may not be able to use simplified treatments which will nevertheless suffice to give us a good deal of information about molecular binding. We may well ask, could we not get fairly complete information about one of the bonds in the molecule, while being content with poor information about the others? The empirical evidence of the chemists all points in the direction of thinking that individual single covalent bonds have a surprising degree of independence of each other. Could we not investigate a single bond, without having to consider the complications of the others?

We can well believe that this could be done; and while no cases have been worked out to test the possibility, let us examine the case of ethane, a fairly simple example, and see how we should treat it. We remember that this molecule consists of two carbon atoms, held together by a single bond, each carbon atom also being bound to three hydrogen atoms. The three hydrogen atoms around a carbon, and the other carbon, form a roughly tetrahedral structure. In other words, the environment of each carbon is something as it is in methane, only with one of the neighboring hydrogens being replaced by the other carbon atom. It is clear, since this molecule is more complicated than methane, that a complete solution will be out of the question unless we can first find how to treat methane. It is also clear that the carbon-hydrogen binding in ethane must be very similar to that in methane, so that once the latter problem is solved, we should be able to draw immediate conclusions about the nature of ethane.

The feature which ethane possesses, however, and which it does not share with methane, is the carbon-carbon bond. The chemists have found that single carbon-carbon bonds in different molecules are remarkably similar, both in the equilibrium distance and in the dissociation energy. Thus there is a good hope that if we could investigate the carbon-carbon bond in ethane, it would give us a good picture of carbon-carbon bonds in more complicated molecules as well. We therefore ask, is it not possible to treat the ethane molecule, introducing enough configuration interaction so that the solution will behave correctly as the carbon-carbon distance is increased from the equilibrium distance to infinite separation, but always keeping the hydrogens bound to the carbons? This might well give us a good account of the carbon-carbon bond.

It might also give us further information. The two triangular groups of hydrogens attached to the two carbon atoms experience only a moderately small torque if they try to rotate with respect to each other. The chemists suppose that the energy has a minimum when the two triangles are rotated 60° with respect to each other, and a maximum when they have the same orientation, for in the latter position the hydrogens on the two carbons are closer to each other than in the former, and they may be expected to repel each other. But the energy difference is small, and it has been well estimated by the chemists. It seems likely that a treatment of the ethane molecule, of the sort we are going to propose, might yield a fairly good value for this energy difference, and hence be something that could be compared to experiment. Either of these two extreme structures has simple symmetry properties, and would not be hard to formulate. As an example, we shall discuss the state that presumably would be the ground state, with the two triangles in an opposed orientation.

Let us then examine this problem, seeing what types of symmetry operations there are, the types of molecular orbitals, and the type of configuration interaction necessary to describe the carbon-carbon bond properly. If we examine the molecule, we see at once that there are twelve different points in space which must be equivalent to each other, in the sense that the potential energy must be equal at each: two points symmetrically located with respect to each hydrogen atom. To get from one such point to another, we then have twelve symmetry operations, including the identity. These symmetry operations fall into six classes: the identity; inversion through the midpoint between the two carbons; rotation through ± 120° (two operations); rotation through ± 120° followed by inversion (two operations); reflection in one of the three planes passing through the axis of the molecule and through hydrogen atoms (three operations); reflection in one of these three planes followed by inversion. Since there are six classes, there must be six irreducible representations. Four of these must be one-dimensional and two two-dimensional, since the only way of writing 12, the total number of symmetry operations, as a sum of six squares of integers, is as $1^2 + 1^2 + 1^2 + 1^2 + 2^2 + 2^2$.

We can understand the nature of these irreducible representations, by comparison with our earlier treatment of the ammonia molecule, in Section 6, Chapter 3. There we had the same rotations and reflections as symmetry operations, but not the combinations of these operations with the inversion. We saw in that section that it was useful to diagonalize the rotation operations about the axis of the molecule. If we do this, we see that the wave function must be multiplied by $e^{2\pi i m/3}$ when we rotate through 120°, where m = 0, ± 1. We set up three different sorts of combinations of the hydrogen 1s functions having these properties: the combinations $\sum(j)\, e^{2\pi i m j/3}\, s_j$, where s_j represent the hydrogen orbitals, and where m = 0, ± 1. Under the reflection operations, the function for m = 0 transforms into itself, while the function for m = 1 transforms into a multiple of that for m = - 1, and vice versa. Thus the combination corresponding to m = 0 forms a basis for a one-dimensional representation of the symmetry group of the ammonia molecule, while the two functions for m = ± 1 form a basis for a two-dimensional representation. Out of these functions, considering the ethane molecule, we now can make sums and differences of the functions on the two H_3 groups.

one of these combinations being of type g, or even under the inversion operation, and the other of type u, or odd under the inversion. We thus have found functions which form bases for two of the one-dimensional irreducible representations, and two of the two-dimensional representations. We can also build up symmetry orbitals of these same types, as we saw when we were discussing ammonia, by using carbon orbitals with $m = 0, \pm 1$, where m represents the component of orbital angular momentum around the axis of the molecule. From each such orbital in one carbon atom, we can build up a g and a u combination.

There are still two one-dimensional irreducible representations to be accounted for, which we did not use in the ammonia problem. Basis functions, or symmetry orbitals, for these can be built up of hydrogen 2p orbitals, rather than 1s orbitals. If we take 2p orbitals having their nodal plane passing through the axis of the molecule, and make up a sum of such orbitals on all three hydrogens, we find that this resulting function transforms differently from any of those which we have considered, in that it is unchanged under the rotations, but changes sign on reflection. We can make g and u combinations of such functions on the two H_3 groups, leading to our two other one-dimensional irreducible representations. Similarly on the carbon atoms, we could get orbitals of the same symmetry by taking a function with $m = 3$, and using the angular function $\sin 3\phi$; this function is unchanged when we rotate through 120°, and changes sign on reflection, thus showing the proper symmetry behavior. Here again we can make g and u combinations of the functions on the two carbons. It is clear that we shall not need symmetry orbitals of this type in the ethane problem, since we have no hydrogen 2p functions, or carbon functions of high enough azimuthal quantum number to have $m = 3$.

As we see from our group theory analysis, these irreducible representations are all that there are for the ethane molecule. Now let us count up to see how many symmetry orbitals of each type we can make up from the available atomic orbitals. For $m = 0$, we can build up both a g and a u combination from the carbon 1s orbitals; from the carbon 2s; from the carbon $2p\sigma$; and from the hydrogen 1s orbitals. When we solve our secular equation for the resulting molecular orbitals, we shall then expect to have a g and a u function made almost entirely from carbon 1s orbitals; a g and a u with the charge concentration largest between the carbons and their adjacent hydrogens, and leading to carbon-hydrogen bonds; another g and u with nodes between carbon and hydrogen, and thus being antibonding as far as the carbon and hydrogen are concerned; and a g and u with major charge concentration between the two carbons, the g function having a bonding nature, but the u having a node midway between the carbons, and thus being antibonding. Similarly for $m = \pm 1$, we can build up a g and a u combination from the carbon $2p\pi$ orbitals, and a g and a u from the hydrogen orbitals. We expect one type of molecular orbital, for either $m = 1$ or -1, and for either g or u type, which shows bonding between the carbons and their adjacent hydrogens, and another showing antibonding. None of these orbitals for $m = \pm 1$ is expected to have much charge in the region between the carbons, or to contribute to the carbon-carbon binding

Of the eighteen electrons in the ethane molecule, we expect that four will be in the g and u orbitals arising from the carbon 1s states. Four more will be in the g and u orbitals of the m = 0 type leading to bonding between carbon and hydrogen. None will be in the carbon-hydrogen m = 0 antibonding orbitals. Eight will be in the m = ± 1 g and u bonding orbitals between carbon and hydrogen, none in the corresponding antibonding orbitals. This leaves two electrons over, to form the carbon-carbon bond. In the molecular orbital state, it is assumed that these will be in the remaining m = 0 orbital of the type leading to carbon-carbon bonding, the g orbital showing charge concentration between the carbon atoms, leaving the corresponding u orbital, which has a node between the carbons, empty.

We see, then, that we have just two electrons to form the carbon-carbon bond, both in a molecular orbital which is symmetric in the plane midway between the carbons; and this situation is precisely similar to that met in the molecular orbital theory of hydrogen. In the hydrogen problem, we remember that to give a correct account of what happened as the internuclear distance increased, we had to take linear combinations of the state in which both electrons were in the symmetric molecular orbital, and of the other state in which both were in the antisymmetric molecular orbital; both these states of the molecule as a whole were of g type, or even under an inversion operation. The situation is precisely the same here. If we take linear combinations of the configuration we have just been discussing, and of the other configuration which differs from it only in that the two electrons forming the carbon-carbon bond are lifted up to the u-type molecular orbital which is antibonding between the two carbons, the configuration interaction problem will be like that in hydrogen, and as in that problem the wave functions will behave correctly in the limit of infinite separation. This simple configuration interaction problem, then, might be expected to give a very good account of the carbon-carbon bond. On the other hand, of course it would do nothing for the carbon-hydrogen bonds, beyond what an ordinary molecular orbital treatment can do. To find what would happen when the hydrogens were removed would require a configuration interaction at least as complicated as in methane. The hope would be that these excited configurations, required to describe the carbon-hydrogen bonds properly, would have relatively small effect on the carbon-carbon binding. Since this problem has not yet been calculated in detail, we cannot evaluate the question as to whether this hope is justified, but calculations which Dr. Meckler is starting should give us the answer.

It is interesting to ask what the two CH_3 radicals will be like, which are left when the carbon-carbon distance increases to infinity. They have the same electronic structure as ammonia, only each has one less electron than in ammonia. We remember that in our discussion of the ammonia molecule, we found that there were two electrons, which we described as a lone pair, extending out along the direction opposite to the side where the hydrogens were located. In the methyl radical, CH_3, there is only one electron in this orbital, and it is the presence of this single electron which leads to the unsaturated nature of the radical. When the two radicals come together to form the molecule, these two electrons form the covalent bond, just like the two electrons in two hydrogen atoms in the hydrogen molecule. The molecular orbital picture of this bond, and its extension by the method of configuration interaction to give a correct picture of the limit of large internuclear distance, should give us a good description of single covalent bonds in general.

Similar simplified treatments can be given for other types of molecules, and on account of the great complication of a correct and complete treatment, it is likely that they will have a great deal of use in studying configuration interaction. Thus Craig(6) has studied the double bond in ethylene by this method. We remember that ethylene has π orbitals of g and u type, formed from a π orbital on atomic type on each carbon. These orbitals hold just two electrons, which go into the bonding type of orbital in the molecular orbital description of the molecule. However, just as in hydrogen and in ethane, we have another configuration of the same symmetry type if both these electrons are in the antibonding type of orbital. As in those cases, a configuration interaction between these two configurations is required to lead to results which are correct in the limit of large internuclear distances. Craig has carried out such a configuration interaction, with good results. Of course, a proper treatment should consider also the σ-electron bond between the carbons, and this has not yet been done. The combined problem of the double bond in ethylene, using the molecular orbital treatment for the C-H bonds as we have sketched for ethane, would yield a problem of the same order of magnitude as the oxygen molecule, which also has a similar double bond.

6. The Directed Orbital and Valence Bond Methods

We have carried the method of molecular orbitals, and configuration interaction between determinantal wave functions made from these molecular orbitals, far enough to see that it has several drawbacks. It is a straightforward method, includes other approaches as special cases, and is certainly the method to be preferred when it can be carried through. Nevertheless, the first obvious drawback is that even with rather simple molecules, such as methane, the number of interacting configurations is so great as to be unmanageable. It would be quite out of the question to use it in its complete form for any but the simplest molecules. The other serious drawback is that it is not suited to display the independence of different covalent bonds, which the chemists find empirically, and which we have mentioned in the preceding section. The simplified procedure described in the preceding section for treating the carbon-carbon bond in ethane suggests that we might be able to go further with the same sort of treatment. In this way we are led to a method of treating molecules by two devices, the directed orbitals and the valence bond wave functions, which has had a certain amount of success. Unfortunately, the uses which have been made of these methods have often been half-empirical, and not well justified, and they have fallen into disrepute. This bad reputation is justified, if the methods are used in the conventional way. Nevertheless they have something to contribute to molecular theory, and in the present section we shall point

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[6] D. P. Craig, Proc. Roy. Soc. (London) A200, 272 (1950).

out the nature of these methods, their history, and then shall try to see how they fit into the type of approach which we have been using in the preceding sections.

These methods had their origin in an effort to apply the Heitler-London method to more complicated molecules than hydrogen. In particular, the simple molecules held together by single covalent bonds, such as ammonia, methane, and ethane, which we have been discussing, certainly do not seem different in their essential structure from hydrogen. We have emphasized that chemical evidence indicates that the various bonds are rather independent of each other. For instance, when a hydrogen atom is removed from methane to form a methyl radical, and this radical combines with another one to form ethane, very little change is produced in the remaining carbon-hydrogen bonds. In turn, if some of the hydrogens of the ethane molecule are replaced by other atoms, for instance a halogen, this still makes little change in the remaining bonds of the molecule. Knowing the geometrical shape of these molecules, we certainly gain the impression that the carbon atom in some sense has four electrons sticking out from it in the tetrahedral directions, and that each of these electrons, rather independently of the others, is capable of forming a single covalent bond with another atom, the bond having many of the features of the hydrogen-hydrogen bond as described by Heitler and London. If the electrons of carbon really do stick out in some such tetrahedral way, it should be possible to describe this in the language of wave functions. Certainly the s and p wave functions of carbon do not have this property, and the combinations of the carbon and hydrogen wave functions which we have described in our molecular orbital treatments of these molecules have no great tendency toward localization; each of the wave functions contributes to the charge density in the neighborhood of a number of bonds, and conversely the charge concerned in a given bond is made up from a number of wave functions.

With these facts in mind, it was pointed out in the early days of molecular theory by Pauling(7) and by the present writer(8) that it is possible to build up one-electron wave functions, or orbitals, which have the desired behavior, by combining s and p wave functions. If we start with a p_x, p_y, p_z, and s function, which we may symbolize merely by p_x, p_y, p_z, s, we may then make four linear combinations of the form $\alpha_{i1}p_x + \alpha_{i2}p_y + \alpha_{i3}p_z + \alpha_{i4}s$, where i takes on the values 1, 2, 3, 4. We can require that these four combinations be normalized and orthogonal; normalization implies four conditions in the α's, and orthogonality six (each of the six angles between pairs of the four vectors must be a right angle). Thus, since we have sixteen α's, and ten conditions on them, we still have six degrees of freedom. One of the combinations, like that written above, represents the sum of a p function pointing in the direction of the three-dimensional vector of components α_{i1}, α_{i2}, α_{i3}, and an s function, and this sum can be set up so as to enhance the p function on one side of the nucleus, and diminish it on the other, so that the orbital will extend out strongly in one direction. Such

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[7] L. Pauling, Proc. [illegible] Acad. Sci. 14, 359 (1928); Phys. Rev. 37, 1185 (1931).

[8] J. C. Slater, Phys. Rev. 37, 381 (1931).

orbitals are called directed orbitals. We cannot have our four orbitals directed in arbitrary directions in space, for we do not have enough constants at our disposal. It takes two quantities to determine the direction of a vector, and hence eight for the four directed orbitals, whereas we have only six constants at our disposal. We may use these, for instance, to determine the directions of three of the orbitals in which case the fourth is specified for us.

In particular, we may choose the a's so that the four orbitals extend out along the four tetrahedral directions from a carbon atom, and in that way we get something which resembles the tetrahedral atom of the chemists. We must notice that the atom is not really tetrahedral. Thus if we assign one electron to each of these four orbitals, and find the total charge density of these electrons, the result is spherical, just as the charge density of three electrons, in the p_x, p_y, p_z states respectively, is spherical. Nevertheless, each orbital is concentrated in a direction which can be chosen to point toward one of the hydrogen atoms in a methane molecule, and it seems attractive to suppose that somehow the binding in methane consists of a covalent bond formed between each of these directed orbitals and the corresponding hydrogen atom, these bonds being formed like the Heitler-London bond in hydrogen, and being essentially independent of each other. In a similar way, we can set up three directed orbitals in ammonia, pointing toward the three hydrogens, and two in water, pointing toward the two hydrogens, and may apply the same sort of argument there. The justification for thinking that the bonds are independent of each other arises simply because the overlapping of the directed orbital forming a given bond, with the other orbital (for instance, a hydrogen orbital) cooperating to form the bond, is much greater than the overlapping of orbitals not pointing toward each other.

The general ideas suggested in the preceding paragraph are rather vague. However, the present writer(9) suggested a method, based on the determinantal method and the general line of argument outlined in previous chapters, for expressing them more precisely. The idea was to formulate something like the Heitler-London method, only to set up a wave function which would describe, not just one covalent bond, but all the covalent bonds in the molecule. Let us illustrate by the water molecule, the simplest one involving two covalent bonds. For convenience, we shall assume that the angle between the two OH bonds is the tetrahedral angle, 109° (though the argument does not depend at all on this assumption, which is only approximately true for the actual molecule). If we have this tetrahedral angle, we can use the same tetrahedral directed orbitals which we should use for methane, two of them being directed toward the hydrogens, which we can denote by orbitals 1 and 2, and the remaining two being in the other tetrahedral directions, and being denoted by 3 and 4. We shall then build up the wave functions of the problem out of these four directed orbitals, the oxygen is orbital, and the 1s orbitals on the two hydrogens.

Our problem is to assign electrons to these various orbitals (instead of to the molecu-

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9 J. C. Slater, Phys. Rev. 38, 1109 (1931).

lar orbitals which we have always used previously), to set up determinantal wave functions corresponding to these assignments of electrons, and to make suitable combinations of determinants to describe the ground state of the molecule. In the water molecule, we have ten electrons. We shall assume that in all determinants which we consider, two of these electrons occupy the 1s oxygen orbitals, and two occupy each of the orbitals 3 and 4 which do not extend toward the hydrogens. These form the description, in this language, of the lone pairs of electrons possessed by the molecule. This leaves two electrons for forming each covalent bond. We expect, then, that each covalent bond will be much as in hydrogen. We remember that in hydrogen, if we have the two atomic orbitals a and b, the Heitler-London state is determined from two configurations: one that in which orbital a is associated with a spin +, orbital b with a spin -, and one which orbital a has spin -, b has spin +. If we set up the determinantal wave functions for the two-electron problem describing these configurations, we remember that the sum of these determinants represents the component of the triplet state having zero component of spin along the axis, while the difference of the determinants represents the singlet state. We ask, cannot we set up such a predeterminated combination of determinants in the present case, representing both covalent bonds?

Since there are four electrons to be assigned to the four orbitals forming the two bonds, and since if we follow the Heitler-London method we shall always assign just one electron to each orbital, we have the same problem of spin degeneracy of four electrons which we have already discussed in Section 2 of the present chapter. For $M_S = 0$, we have six possible assignments of spins to orbitals. If we use the same table as in that section, but now denote our orbitals as o_1, h_1, o_2, h_2, to stand for the oxygen and hydrogen orbitals forming bonds 1 and 2, then these assignments of spin are given in Table XVI. We now remember that according to our study of the problem of spin degeneracy of four electrons, we found that there were two singlet states. We can get at them in the following way: we set up the combinations 1 + 6, 2 + 5, and 3 + 4 of the states above. The sum of these represents the quintet function; but any two linear combinations of these functions which are orthogonal to each other, and orthogonal to the quintet, may be taken as representing singlets. Let us see if we can form by inspection a singlet function which corresponds to the desired covalent binding.

Table XVI

State	o_1	h_1	o_2	h_2
1	+	+	-	-
2	+	-	+	-
3	+	-	-	+
4	-	+	+	-
5	-	+	-	+
6	-	-	+	+

If we had only the two functions o_1 and h_1, between which a bond was to be formed, we should set up the two configurations +- and -+, and we know that the singlet state would be the difference of these two determinants. A similar thing would occur if we only had the functions o_2 and h_2. We now notice that we can set up the combination of functions 2 - 4 + 5 - 3. This in the first place is a combination of (2 + 5) and (3 + 4), and can be shown to be orthogonal to the quintet, so that it represents a singlet. Next, it has in each case a + and - spin on each bond, which it would not do if the states 1 and 6 were included. The functions 2 and 4, which correspond to the same spins on o_2 and h_2, but opposite arrangements of spin on o_1 and h_1, appear with opposite sign. So do the functions 3 and 5, which have the same relationship to each other. Similarly, the functions 2 and 3 correspond to the same arrangement of spins on o_1 and h_1, but different assignments to o_2 and h_2, and they appear with opposite signs, as do 4 and 5. There is thus a symmetry about this function 2 - 4 + 5 - 3, which suggests the Heitler-London ground state wave function. It is this particular combination of determinantal wave functions which is called the valence bond wave function for this problem.

The virtue of this valence bond wave function is shown if we consider a limiting case in which the two bonds are really independent of each other. That is, we assume that the pair of functions o_1 and h_1 on the one hand, o_2 and h_2 on the other, are so completely independent of each other that any integral of energy or orthogonality integral between functions some of which belong to the one pair, some to the other, vanishes. In this case, it is easy to work out the matrix component of energy with respect to the valence bond wave function, and we find that we are led exactly to the problem of two independent valence bonds, each handled by the Heitler-London method. The reader can verify this for himself, taking for instance the case where o_1 and h_1 refer to two hydrogen atoms forming a molecule, and o_2 and h_2 refer to two other hydrogen atoms forming a molecule so far from the first that there is no physical interaction between them.

The use of the methods of directed orbitals, and of valence bond wave functions, from this point on, has generally been entirely unjustified, on account of unwarranted assumptions. It has been assumed that the directed orbitals are sufficiently independent of each other so that this result, which we have just mentioned, would hold in real molecules, the total energy being the sum of two energies representing the two covalent bonds, each being similar to the energy of hydrogen as predicted by Heitler and London. The unwarranted assumptions have generally extended further than this: very often the overlap integrals met in the Heitler-London method have been disregarded, though we saw in Chapter 2 that they were actually large. A large literature has been built up based on these assumptions, and it can hardly be regarded as anything but an empirical development, without theoretical justification. If we actually set up the valence bond wave function, and compute its diagonal energy, we find, as the writer showed in his original paper on the subject, that it is extremely complicated, involving three- and four-center integrals of complicated type, which are by no means negligible in comparison with the terms which resemble the calculation of the Heitler-London method. It seems not unlikely that a correct calculation of the energy of this valence-bond wave function would yield a fairly good value for the energy of the molecule, but very few calculations have been made without the unwarranted neglect of terms which we have mentioned. The reason is partly the difficulty of calculating three- and four-center integrals, which are only now coming to be calculated with any accuracy.

In spite of the crudeness of the way in which the valence bond method has generally been used, still an extensive literature has grown up around some aspects of its formalism. These aspects are largely those concerned with the solution of the spin degeneracy problem. If we return to Table XVI, we have seen that the combination of functions 2 - 4 + 5 - 3 yields a valence bond function indicating bonds between orbitals o_1 and h_1, and between o_2 and h_2. If we just regard these as four orbitals of a general form, there are two other ways in which we could draw the bonds between them. These are indicated in Fig. 7, where we show the orbitals as points, the bonds as lines connecting pairs of points. We see that we can draw the bonds just as well between o_1 and o_2, h_1 and h_2; or between o_1 and h_2, o_2 and h_1. We can set up combinations of our functions 1 - 6 of Table XVI which express these other valence bond functions. Thus the combination expressing the case where the bonds are between o_1 and o_2, and between h_1 and h_2, is - 1 + 3 + 4 - 6, and that expressing the case where the bonds are between o_1 and h_2, o_2 and h_1, is 1 - 2 - 5 + 6. We have, then, three valence bond functions, each representing a singlet state; and yet we know that there are only two singlet states concerned in the problem. This would indicate that our three functions are not linearly independent, and this is in fact the case. We can see this at once by adding them: we have (2 - 3 - 4 + 5) + (- 1 + 3 + 4 - 6) + (1 - 2 - 5 + 6) = 0. In other words, since the three functions add to zero, any one of them is a linear combination of the other two.

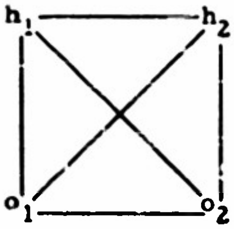

Fig. 7

Possible ways of drawing valence bonds in problem of four orbitals.

If, then, we make two orthogonal linear combinations of two of these functions, say of the ones (2 - 3 - 4 + 5) and (- 1 + 3 + 4 - 6), these functions can form the starting point for a calculation from which we shall find the two singlet states, and if we find diagonal and non-diagonal matrix components of energy between these two functions, we shall have a quadratic secular equation for these two singlets. In other words, the valence bond functions form a starting point for the problem of spin degeneracy. They are not a very convenient starting point, for they are not orthogonal to each other. They clearly cannot be, since the three valence bond functions are linearly dependent, they therefore represent three vectors lying in a plane, and if we have three unit vectors in a plane adding to zero, as these do, we can show easily that these vectors must make angles of 120° with each other, so that no two of them are orthogonal. It is not very hard to set up orthogonal linear combinations of them, however, so that this is not a very great difficulty in the way of using this method to solve spin degeneracy. It is not, however, the simplest way to do it.

Part of the literature of valence bond wave functions has been devoted to the general question of how many of the possible ways of drawing valence bond functions are linearly independent, as two of the three possible ways are linearly independent in the problem of four electrons. Rumer, Wheland, and many others, have contributed to this study, and the references are given in the bibliography. It turns out that there is a simple and general rule telling how many linearly independent valence bond wave functions there are in any particular case. We make a diagram like that of Fig. 7, but omit any sets of bonds whose corresponding lines cross each other, as the bonds between o_2 and h_1, o_1 and h_2, cross each other in the figure. The remaining sets of bonds (two sets in our case) form a linearly independent set. Since we have seen that this method of valence bond wave functions forms one way of solving the problem of spin degeneracy, in particular for finding the singlet states (which alone are expressible in terms of valence bond functions) we see that this type of formalism can have value for other problems than the application to covalent binding, though as we have mentioned earlier this does not seem to be the simplest way to handle problems of spin degeneracy.

The formalism of which we have been speaking, however, in spite of its legitimate applications, has often been used in the literature in the unjustified approximate way which we have already mentioned. The interaction of the various wave functions derived from valence bond methods, which corresponds to the interaction of the various singlet states of a molecule to form the ground state, is one of the interactions which Pauling has termed resonance. A large literature has grown up in which the corresponding secular equations are solved, but with the crudest assumptions possible concerning the corresponding matrix components of energy. We have already mentioned the type of approximation which has been made in computing the diagonal matrix component of energy with respect to a valence bond function, with neglect of non-orthogonality, and with the assumption that different bonds are largely independent of each other. The same sort of approximations have been made in computing the non-diagonal matrix components of energy between the various valence bond wave functions, and the resulting secular equation has then been solved. It is clear from the remarks that have been made already that the writer does not feel that these approximations made in the calculation of the matrix components are valid enough to give any quantitative significance to the results of these calculations.

We have mentioned that one reason why all these approximations have been made is simply the difficulty of making the exact calculations. The method which we are outlining is essentially a generalization of the Heitler-London method, and we have seen in Chapter 2 that this method is much less convenient than the method of configuration interaction using molecular orbitals, in that it deals with non-orthogonal atomic and non-orthogonal determinantal functions. We may reasonably ask, could we not introduce a configuration interaction method using directed orbitals, possessing the advantages of the Heitler-London method in that it treated the various bonds as being largely independent of each other, but possessing the convenience of dealing with orthogonal orbitals? In the next section we shall show that something of this sort may well be possible, though it has not yet been tested enough to make sure of its validity.

Quite aside from these formal difficulties connected with the extension of the Heitler-London method based on directed orbitals and valence bond functions, there are certain fundamental shortcomings of the method, which must be corrected in order to get anything closely approaching the truth. These shortcomings arise from the neglect of ionic or polar states of the molecule. In Chapter 2, we have seen that inclusion of ionic states of the H_2 molecule, in which one atom forms a positive ion the other a negative ion, makes a practically negligible improvement with respect to the Heitler-London calculation, in which this is disregarded. In a heteropolar molecule, however, one in which the bonds are formed between unlike atoms, we expect a much greater effect to arise from the polar states. Thus, if we take an extreme case such as the HF molecule, the calculation corresponding to the Heitler-London method would suggest that the molecule should be unpolarized, the hydrogen atom always carrying a single electron, and the fluorine atom being always neutral. We can well imagine, however, on account of the large dipole moment which this molecule is known to possess, that a polar configuration, formed from a proton and a negative fluorine ion, might represent a configuration which would be represented rather strongly in the actual ground state of the molecule. The straightforward valence bond calculation, based on the sort of spin degeneracy problem indicated in Table XVI, takes no account of such polar states, and this is a serious shortcoming of the method.

It is, of course, entirely possible in principle to extend the valence bond method to the case where we include polar states, just as it is possible in hydrogen to consider interaction with ionic states in the framework of the Heitler-London theory. If we include all possible polar states, and consider the interaction, using the valence bond method of setting up unperturbed singlet wave function, but then solving a secular equation between all states of the same symmetry properties, we shall end up with just as general a solution as that found by configuration interaction starting with molecular orbitals, and the answers will be identical. The method is likely to be more complicated, however, on account of the non-orthogonal nature of the valence bond functions, and if such a complete configuration interaction calculation is to be made, a straightforward calculation using molecular orbitals is probably the simplest method, just as the problem of configuration interaction in hydrogen is more conveniently set up in terms of molecular orbitals, or of orthogonalized atomic orbitals, than in terms of Heitler-London non-ionic and ionic states.

A major reason for the inconvenience of the Heitler-London method has been pointed out in Chapter 2: the Heitler-London functions representing non-ionic and ionic states are by no means orthogonal to each other, and in fact as the internuclear distance decreases they become much more nearly identical than orthogonal functions. Such a situation always greatly complicates the numerical use of the functions for solving problems of configuration interaction. These orthogonality difficulties, which are so serious that the actual calculations using Heitler-London functions including ionic states are practically impossible to carry out with any molecule of any degree of complication, have simply been glossed over by the writers who use this method, hidden by their unjustified approximations involved in their calculations of matrix components.

7. Directed Orbitals and Configuration Interaction

The criticism which we have given in the preceding section indicates the reasons for feeling that the method of directed orbitals, coupled with the use of valence bond wave functions, does not form a useful approach to the problem of molecular structure. However, certain features of the method, or of the reasoning behind its original suggestion, remain valid, and we shall ask in the present section how it could be adapted to the method of configuration interaction, with possible use to simplify that method. We can see at the outset the form which any simplification must take. Whatever orbital functions we start with, we shall find the same number of interacting configurations to lead to any particular state of the molecule. It might be, however, that by using particular orbitals, such as the directed orbitals, we might find that the wave functions of some of these interacting configurations were represented in the linear combination representing the ground state with small enough coefficients so that they could be disregarded. If we could be sure from the outset that this would be the case, we could disregard these configurations from the beginning, and thus effectively reduce the number of interacting configurations.

With this in mind, let us analyze the way in which we would apply the method of directed orbitals to configuration interaction problems, and see if such a simplification is likely. We can investigate the general situation without going into details, and we shall do this first, before looking into the precise way of carrying out the method. We note in the first place that the valence bond method, in which we use only one valence bond wave function without configuration interaction (that is, without resonance), gives us a unique wave function for the molecule. We cannot hope to do this if we are using configuration interaction. We remember that in the molecular orbital treatment of hydrogen, using configuration interaction, we needed two wave functions, in one of which both electrons were in the symmetric molecular orbital, and in the other of which both were in the antisymmetric orbital. Interaction of these two led to the ground state. If the atoms had not been identical, we should have needed still another wave function, that in which one electron was in the bonding, and the other in the antibonding, orbital. The reason for the three is that in hydrogen this last combination results in a ${}^1\Sigma_u$ and a ${}^3\Sigma_u$ state, the first two combinations in two ${}^1\Sigma_g$ states, and the Σ_u and Σ_g states are non-combining; whereas with unlike atoms, there is no inversion symmetry corresponding to the distinction between the g and u states, so that we have three singlets which can all combine with each other. Thus, we cannot hope to treat a bond between unlike atoms by configuration interaction, without using three configurations per bond, and solving the resulting secular equation for the singlet states (which normally will be the ground state).

We might expect, then, that we could get some sort of solution of the covalent bonding problem by using three configurations per bond, in some sense. We note at the outset that this can mean a great reduction in the number of configurations, compared to the molecular orbital method. The reason is that we are tacitly assuming that we shall assign two electrons to each single bond, whereas the general configuration interaction problem, if we set it up in terms of directed orbitals, would include the possibilities that we have every number from zero to four electrons in each bond. In other words, the real simplification which seems plausible to us, if we are thinking in terms of directed orbitals, arises from the probability that the configurations corresponding to any numbers of electrons per bond different from two will appear in the final configuration interaction with small coefficients.

We cannot tell whether this situation really holds or not, without testing it out in some actual case. It is for this reason that the calculation which Koster and Schweinler are carrying out for water, which we have mentioned earlier, can be very valuable. They will get the exact solution of the complete configuration interaction problem. From the resulting ground state wave function, it will be easy to find the contributions from those states corresponding to just two electrons per bond (and therefore just four lone pair electrons). If these states really lead to a practically correct wave function, we should have a good deal of confidence that a similar simplification held in general, while if the assumption fails significantly to be justified for water, we should expect it to fail in other cases as well, and in that situation the method of directed orbitals would have no particular merit in simplifying the problem. The answer cannot be given until the actual case is worked out.

Let us proceed to see just how the method of directed orbitals could be incorporated into our procedure for handling configuration interaction. We shall start by considering the case of methane, since this is an interesting case in which the simplification resulting from the directed orbital method might be quite profound. We shall first describe how a set of orthogonal directed orbitals could be set up, suitable for use as a starting point for the configuration interaction problem; then we shall describe how to carry out that configuration interaction.

In describing these orthogonal directed orbitals, we could start with the type of orbitals described in Section 6. We could set up four linear combinations of the carbon 2s and 2p atomic orbitals, directed along the four tetrahedral directions. We could call these combinations c_1, c_2, c_3, c_4. Then we should have four hydrogen 1s orbitals, which we could call h_1, h_2, h_3, h_4. These are not convenient orbitals to use, however, for though the carbon orbitals $c_1 \ldots c_4$ are orthogonal to each other, by their method of construction, they are not orthogonal to the hydrogen orbitals, and these in turn are not orthogonal to each other. Our first step must be to set up orthogonal linear combinations of these functions, which have the required tetrahedral symmetry. This can be done in an infinite number of ways, and to get a unique way, and one adapted to the problem, it is better not to start with these carbon and hydrogen orbitals at all, but instead to describe the procedure in terms of the molecular orbitals.

7. DIRECTED ORBITALS AND CONFIGURATION INTERACTION

We remember that when we were discussing the molecular orbitals for methane, we showed that they had symmetry properties similar to s or p functions of an atom. That is, we had a one-dimensional irreducible representation whose functions transformed into each other under any of the operations of the tetrahedral group, and a three-dimensional irreducible representation whose functions transformed into each other like the three degenerate p functions. As symmetry orbitals of the s-like type, we had orbitals formed from the carbon 1s, carbon 2s, and the combination of the hydrogens which had proper symmetry, and the resulting molecular orbitals resembled the carbon 1s, a bonding combination of the carbon 2s and the hydrogens, and an antibonding combination. Similarly the molecular orbitals of the p-like type were a bonding and an antibonding combination of carbon and hydrogen orbitals. Now we can take the bonding orbitals of s-like and p-like type, and make four linear combinations of these by just the same procedure used to set up the directed orbitals of carbon, which we described in the preceding section. Similarly we can take the antibonding orbitals of s-like and p-like type, and make four directed combinations. The result will be a 1s-like orbital, four bonding directed orbitals, and four antibonding directed orbitals, all orthogonal to each other. Since the molecular orbitals are approximated as linear combinations of atomic orbitals, and these directed orbitals we have just been describing are linear combinations of molecular orbitals, they are also linear combinations of atomic orbitals, and could be described directly in that language, but the procedure we have just stated is the simplest way of visualizing them. These functions, of the type we have just described, are related to the ordinary directed orbitals c_1, c_2, c_3, c_4, and to the hydrogen orbitals h_1, h_2, h_3, h_4, much as the hydrogen molecular orbitals $a \pm b$ are to the atomic orbitals a and b in the hydrogen problem.

Before using these bonding and antibonding directed orbitals, let us see a little more in detail just what their relation is to molecular orbitals. The molecular orbitals are set up in such a way as to form basis functions for irreducible representations of the symmetry group of the molecule. They diagonalize the one-electron energy of the self-consistent field. The directed orbitals do neither of these things. The four tetrahedrally directed orbitals form a basis for a reducible representation of the symmetry group; we can get at the irreducible representations out of which it is composed by undoing the linear transformations which produced the directed orbitals out of the s- and p-type molecular orbitals. Furthermore, the directed orbitals do not diagonalize the one-electron Hamiltonian. If we solve a secular equation to diagonalize this Hamiltonian, of course we come back to the s- and p-type orbitals, with their appropriate one-electron energies. We can easily find the non-diagonal matrix components of energy between these directed orbitals, but shall postpone this until a later time, when we shall take up the theory of such functions much more in detail.

The characteristic which these directed orbitals have, from the point of view of group theory, is that under every symmetry operation of the group, each directed orbital either transforms into itself, or into another directed orbital. Thus, the two-fold or three-fold rotations of the tetrahedral group interchange the directed orbitals. Orbitals which have these properties are called equivalent orbitals in recent work by Lennard-Jones(10) and collaborators. Their general theory, and the matrix components of energy between them, have been discussed in a recent paper by Koster.(11) The great importance of such orbitals comes not so much in molecules, useful as they are there, but in crystals, and for this reason we postpone their discussion until we are dealing with crystals. There the Wannier function, orbitals localized on single atoms of the crystal, form examples of equivalent orbitals which transform into each other by the symmetry operations which are translations in the lattice. These functions are invaluable in discussing properties of a crystal which take place in a localized volume, and we shall postpone our general discussion until we are concerned with that problem.

Let us now go back to the directed bonding and antibonding orbitals in methane. We can use them, just as well as the original molecular orbitals, in setting up the problem of configuration interaction. Let us first observe that the determinantal wave function representing the molecular orbital ground state will be just the same using directed orbitals that it is using molecular orbitals. In terms of molecular orbitals, the molecular orbital ground state arises when two electrons are in the 1s carbon orbital, two in the s-type bonding orbital, and two each in the three p-type bonding orbitals. But the directed bonding orbitals are linear combinations of the s-type and p-type bonding orbitals. We know that a determinantal wave function is not affected by introducing new orbitals which are linear combinations of the orbitals out of which it is constructed, and that is just the situation which we have here.

In other words, as far as the molecular orbital ground state is concerned, there is no real difference whether we use molecular orbitals or directed bonding orbitals. There is a formal difference, which has been pointed out by Lennard-Jones and his collaborators, in the references made above. This formal difference arises because the various coulomb and exchange integrals between directed orbitals look quite different from those between molecular orbitals, and it is natural that, since the directed orbitals are much more concentrated, these coulomb and exchange integrals between electrons in the same directed orbital will be much larger than if we use molecular orbitals, while the integrals between electrons in different directed orbitals will be smaller. Lennard-Jones and his associates see in this fact the justification of the use of directed orbitals, feeling that in this way the concentrated nature of the covalent bond is expressed. The writer feels that the more real justification of the use of directed orbitals may come when we are considering configuration interaction, in the way to be described immediately.

When we come to considering configuration interaction by means of directed orbitals, we must proceed rather differently from the way we did when we used molecular orbitals, on account of the different symmetry properties. We know that we are looking for singlet configurations which possess the full symmetry of the group, transforming into themselves under

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[10] J. E. Lennard-Jones, Proc. Roy. Soc. (London) A198, 14 (1949); J. E. Lennard-Jones and J. A. Pople, Proc. Roy. Soc. (London) A202, 166 (1950).

[11] G. F. Koster, Phys. Rev. 89, 67 (1953).

Table XVII (con'd.)

	a_1	b_1	a_2	b_2	a_3	b_3	a_4	b_4
13.		2		2	1	1	1	1
14.		2		2		2	1	1
15.		2		2		2		2

Of the fifteen assignments of electrons to bonds in this table, those in which each orbital has two electrons, and those in which there are just two orbitals with one electron each, will each lead to one singlet. Those with four orbitals with one electron each will lead to two singlets, as always in a spin degeneracy of four electrons. Those with six orbitals with one electron each will lead to five singlets, as in the spin degeneracy of six electrons, but closer examination of the wave functions shows that only two have the correct symmetry for the ground state, and those with eight orbitals with one electron each will lead to 14 singlets, of which three prove to have the correct symmetry. Thus there will be 22 singlets of the correct symmetry arising from the configurations in Table XVII. We have thus achieved a great reduction compared with the total of 104 configurations; but we must remember that this reduction is only justified if the coefficients multiplying the remaining 82 configurations, which represent cases with different numbers of electrons on the various bonds, are really small, and this can be verified only by computation.

It is not impossible that the reduction in the order of configuration interaction can be carried considerably further than this. Let us consider one of the configurations in Table XVII, which contains spin degeneracy between more than two electrons; for example, state 4, involving spin degeneracy between four electrons. It is possible that there is really some virtue in the valence bond function, which assigns the spins as if bonds were being formed between certain pairs of electrons. It is possible, in other words, that of the two singlet functions which can be set up from the spin degeneracy problem in configuration 4, the valence bond function assigning the interaction to the bonds between a_1 and b_1, and between a_2 and b_2, will come in with a considerably larger coefficient than the other singlet function which we could form, orthogonal to this valence bond function. If such a situation were to hold in general, it might prove to be true that in each of the configurations in Table XVII showing spin degeneracy, the most important contribution would come from the valence bond function, and in that case we might be able to disregard the others, and use only 15 configurations, one formed from each of the entries in Table XVII. If this proved to be possible, it would be a useful reduction indeed in the order of the configuration interaction. We note that all those configurations in Table XVII showing spin degeneracy involve one electron in a bonding orbital, one in an antibonding orbital, of the same bond. Thus, these are the configurations which would be completely missing if the bonds had the inversion symmetry characteristic of hydrogen, so that configurations with one electron in an antibonding and one in a bonding orbital were non-combining with configurations in which both electrons were bonding, or both antibonding. This might suggest that in the actual case the coefficients of all these configurations were small, so that we should be doing less violence to the problem than otherwise by using only the valence bond configuration.

As we have emphasized, this section is highly speculative, merely suggesting directions in which one might look to find configurations which did not contribute greatly to the configuration interaction problem. Calculation will have to be made, on simple cases, to see whether any of these suggestions are justified enough to make such methods useful. We have mentioned that the calculation now being made for water may well furnish a case for testing these assumptions. Let us therefore examine how the water problem would look, when set up in terms of directed orbitals, so as to see what we are to look for.

In the first place, if our hypothesis is correct that the important configurations are those in which each bond has just two electrons, we should conclude at once that in the important configurations there should be two π electrons, in the notation which we used earlier in discussing water. Thus in Table XII, we should conclude that the only important configurations were those arising from the states marked 4, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, in which there are two π electrons. These eleven states result in twelve out of the eighteen configurations of the molecule, and the first test of the calculations will be to see if the coefficients of the remaining six configurations are really small.

Proceeding further, we can get a table of configurations for water, like the table which we have made for methane, by simply leaving out the columns marked a_3, b_3, a_4, b_4 in Table XVII, and by including only the first six states from that table. These six states lead to seven singlets, out of the twelve. The remaining five singlets arise from the assignments of electrons to bonds shown in Table XVIII.

Table XVIII

Configurations for Water, Involving More or Less than Two Electrons per Bond

a_1	b_1	a_2	b_2
2	1	1	
1	2	1	
2	1		1
1	2		1
2	2		

If the coefficients of the five configurations described in this table prove to be small, we shall be justified in our hypothesis that the important configurations are those in which there are just two electrons in each covalent bond, and should feel a certain amount of assurance in using this same hypothesis in more complicated molecules, in which the complete configuration interaction problem was too hard to solve.

Until some such test as this is made for the method using directed orbitals, we must regard this method with a good deal of suspicion. It is by no means obvious that this method, or in fact any simplification of the general method of configuration interaction which has yet been suggested, will really prove to have enough quantitative validity to justify its use. We may only hope, however, that some such simplification will be found as a result of the detailed calculations which are now being made.

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In the succeeding pages we present a bibliography of papers on the theory of the electronic structure of molecules. The writer hopes that this bibliography will be useful, but nevertheless presents it with a good deal of apology. It is a result of rapid compilation, and in a great many cases papers have been included, or in some cases excluded, without taking time to assess adequately whether they really belonged or not. The bibliography was constructed largely by the simple method of going through a given paper, noting the references made by the author, going through those references, noting their references, and so on. This method is likely to lead one rather far into sidelines, and there are a good many papers listed, largely on the application of molecular orbitals to detailed chemical problems, which are rather far from the main topics of this report. Nevertheless the reader of the report may want to explore some of the directions in which progress has been made, and this bibliography should help him in doing so.

The general field included, as stated above, is the theory of the electronic structure of molecules. Very few experimental papers have been included (except perhaps by oversight) except those in which there were interesting applications of theory. Papers on the nuclear vibrations of molecules have not in general been included, unless there seemed some particular reason why they might be of interest to readers of the report. Similarly papers on the theory of atomic spectra, on general quantum mechanics, and on the theory of the electronic structure of solids, have not been included, except in a few special cases, though it is hoped to include a bibliography similar to the present one, dealing with solids, in the companion report to this, which will deal with the theory of solids. When there was a question of including a given paper or not, however, the general tendency has been to include it. It was felt that this would probably detract less from the usefulness of the bibliography than to omit potentially useful papers.

The writer is well aware that the method used for compiling the bibliography is liable to lead to very important omissions. As a conspicuous example, it has not led to inclusion of the Russian literature, an omission which the writer regrets, and does not justify on any other grounds than that he has put in all the time on the preparation of the bibliography that he can afford at the moment, and feels that the result, though imperfect, may yet be better than nothing. He would be much obliged if readers would inform him of conspicuous omissions. They are practically sure to be a result of oversight, and not of a conscious desire to slight any work.

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